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RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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NEW BOOKS AND OTHER PUBLICATIONS

1942 YEAR BOOK OF THE LOS ANGELES RUBBER GROUP. Published by the Group (Secretary, C. R. Wolter, Kirkhill Rubber Co., 811 West 58th St., Los Angeles, California). 8½ x 11 in. 16 pp.

This is the first of a series of annual year books to be issued by the Los Angeles Group, Division of Rubber Chemistry. It is dedicated to Edward L. Royal of H.M. Royal, Inc., "in appreciation of his unselfish devotion". The book contains a list of past chairmen of the group, current officers and committee members, by-laws, names and addresses of all members, and list of rubber manufacturers and suppliers to the industry located in the Pacific coast area. The latter two lists were reproduced from the 1941 Rubber Red Book. [From *The Rubber Age* of New York.]

INDUSTRIAL CHEMISTRY OF COLLOIDAL AND AMORPHOUS MATERIALS. By Warren K. Lewis, Lombard Squires, and Geoffrey Broughton. Published by The Macmillan Co., 60 Fifth Ave., New York City. 6¼ x 9¼ in. 540 pp. $5.50.

This book is a comprehensive text on the industrial chemistry of colloidal and amorphous materials, including rubber, paper, leather, ceramics, textiles, and synthetic resins and plastics. It accomplishes a double purpose in that it gives the reader not only a description of the methods practiced in various industries but also an insight into the underlying phenomena so that he can appreciate the potentialities and limitations of processes and materials. Thus, it serves to develop the reader's capacity for controlling and using certain processes and materials, presuming that the reader has a background of chemistry and is concerned with the handling of colloidal and amorphous materials.

As an indication of the treatment given to the various industries using the materials covered by the book, the chapter on rubber is an excellent example. This chapter contains data on latex, chemical properties of rubber, physical properties of raw rubber, milling, vulcanization, accelerators, fillers and reinforcing agents, production from latex, and aging. Data on reclaimed rubber, and what the authors term artificial rubber, are included. The change which occurs in rubber from collection to finished product is ably told. Industrial applications are confined to the latter portion of the book, the first part being devoted to the presentation of basic material, including such subjects as the structure of liquids,

viscosity, surface tension, adsorption, the electrochemical behavior of colloids, etc.

The book is an outgrowth of personal, practical experience which covers a thirty-year period. It embodies the results of twenty-five years teaching the subject at the Massachusetts Institute of Technology. It contains twenty-one chapters and a comprehensive subject index. Brief bibliographies, which are intended to give an introduction to the literature that will emphasize the breadth of the various fields and the differences in approach, follow each chapter. [From *The Rubber Age* of New York.]

GUAYULE. The General Tire & Rubber Co., Akron, O. 16 pages.

This illustrated booklet describes the development of guayule cultivation in Mexico and California during the past fifty years. The extraction process, deresination, and the McCallum-and-Spence cultivation methods are discussed. [From the *India Rubber World.*]

CLEANING, REPAIRING, AND STORAGE OF HOUSEHOLD RUBBER GOODS. Helen G. Wheeler. Division of Textiles and Clothing, Bureau of Home Economics, United States Department of Agriculture, Washington, D. C. 21 pages.

The causes of deterioration of rubber are briefly discussed and methods of cleaning, disinfecting, preserving, and repairing such articles as footwear, clothing, garden hose, electric cord, gloves, druggists' sundries, rubber flooring, and garments containing rubber thread are described in this mimeographed government release. [From the *India Rubber World.*]

COMPOUNDING OF BUNA-S. R. T. Vanderbilt Co., 230 Park Ave., New York, N. Y. 8 pages.

This report presents the material on which was based the address of A. A. Somerville at the meeting of the Detroit Rubber and Plastics Group, Inc., May 8. It covers laboratory work and observations on the processing, general compounding, loading, and vulcanization of Buna-S. Data on percentage permanent set, tear resistance, impact resilience, Shore hardness, stress-strain, tensile, and other properties are shown in comparison with those of natural rubber compounds. Conclusions based on the tests are briefly summarized. [From the *India Rubber World.*]

PLASTICS DIGEST. Vol. 1, No. 1. Jan., 1942. Plastics Publishing Co., P. O. Box 523, New Brunswick, N. J. 39 pages.

This abstracting periodical in the fields of plastics and synthetic rubber covers United States, Canadian, and foreign developments. The various departments include abstracts of general and patent literature in chemistry, research, testing, analysis, and technology; news; trade literature; and new applications. [From the *India Rubber World.*]

RESINS-RUBBERS-PLASTICS. A looseleaf abstract service. Edited by H. Mark and E. S. Proskauer. Published by Interscience Publishers, Inc., 215 Fourth Ave., New York, N. Y. Subscription Price: $35.00 per year.

The first issue of this abstract service, devoted to the complete field of synthetic resins, rubbers and plastics, including the scientific aspects of cellulose and fiber chemistry, consists of 33 pages, each 6½ x 9½ inches in size, and contains the table of contents of the service and a number of abstracts from the January,

1942, issues of various scientific and technical periodicals. The abstracts are fairly comprehensive, containing most of the data and facts of the original paper, with important graphs, curves and apparatus reproduced. The abstracts themselves are subdivided for convenience of the user.

File numbers are provided for each abstract. A key to the file numbers indicates that the reference book will be divided into two parts—General and Special. The General Part will combine all information which does not refer to a specific chemical compound or group of substances, but which is characteristic of or important to a sector of the reviewed field. Main subheadings of this part are Physical and Chemical Properties, Physical and Chemical Methods and Testing, Chemical Statics and Kinetics, Manufacture, Moulding and Vulcanization, Finishing of Products, and Applications.

The Special Part will be subdivided according to substances or groups of substances, such as acrylic resins, cellulose plastics, and butadiene rubbers. Within each section of this part, the same scheme is employed as for the General Part. This means, as an example, that all information on the tensile strength of chloroprene rubbers will be coördinated under the same filing number in the same section of the binder, which is supplied at an extra cost of $3.00. [From *The Rubber Age* of New York.]

THE TECHNOLOGY OF NATURAL RESINS. By C. L. Mantell, C. W. Kopf, J. L. Curtis, and E. M. Rogers. Published by John Wiley & Sons, Inc., 440 Fourth Ave., New York City. 6 x 9 in. 506 pp. $7.00.

This book fills the gap in the literature concerning the technology of certain of the natural resins, including damar, copal, East India, and related resins, their properties, their applications, industrial uses and development. The treatment throughout the book is more practical than theoretical or even scientific. The place of the natural resins in commerce is continually stressed. The book has twenty-six chapters, complete author and subject indexes, and a valuable appendix which includes native designations of natural resins. [From *The Rubber Age* of New York.]

OCCUPATIONS IN RUBBER. American Job Series. No. 26. Charles W. Ufford. Science Research Associates, 1700 Prairie Ave., Chicago, Ill. 49 pages.

The coördinated material in this publication offers to job seekers effective orientation in the development and manufacturing processes of the rubber industry. Various types of work are described, and an occupational chart shows the wide possibilities for employment. The requirements for factory, supervisory, technical, merchandising, and foreign positions are outlined. Occupational hazards, hours and earnings, advancement opportunities, the future of the industry, and other factors are surveyed, and it is pointed out that mechanical goods are a rapidly growing branch of the industry. [From the *India Rubber World.*]

RUBBER DATA FOR THE ENGINEER. British Rubber Publicity Association, 19 Fenchurch St., London, E.C.3, England.

This handy circular chart, on proper alignment of an arrow, shows the properties of various types of compounded rubber and their applications. It is supplied gratis. [From the *India Rubber World.*]

THE DEVELOPMENT OF AMERICAN INDUSTRIES. Revised Edition. Edited by John George Glover and William Bouck Cornell. Prentice Hall, Inc., 70 Fifth Ave., New York, 1941. Cloth, 6 by 9¼ inches, 1005 pages. Illustrated. Tables and charts. Indexed. Price $5.50.

The material, prepared and written by specialists in thirty-nine industries, including rubber, provides a readable and useful history of industrial economy in the United States. Each chapter surveys the growth, the raw materials used, manufacturing and marketing methods, important products, employment, and possible future developments of an industry. Social and economic factors during the past ten years and the effects of legislation are explained. Changes in production methods are discussed and new products described.

The informative chapter, "The Rubber Industry", written by A. L. Viles, president of The Rubber Manufacturers Association, Inc., broadly surveys all important phases of the subject. The geographical location of the manufacturing industry is discussed, with emphasis on the recent tendency toward decentralization for economy in distribution. Methods of rubber manufacture are briefly described, and the marketing of tires, boots and shoes, druggists' sundries, mechanical goods, rubber flooring, rubberized fabrics, and heels and soles outlined. A chart of the organization of a typical rubber company and the 1937 Census of Manufactures showing production units and sales value by types of rubber products are valuable aids to the author's discussion. Mr. Viles gives the total estimated world-wide investment of American rubber companies as $1,250,000,000, and suggests that developments having possibilities for increased future production are foamed rubber, parts for motor vehicles and aircraft, and pneumatic tires for farm equipment. [From the *India Rubber World*.]

THORPE'S DICTIONARY OF APPLIED CHEMISTRY. VOLUME V. FEHLING'S SOLUTION TO GLASS. J. F. Thorpe and M. A. Whiteley. 4th Ed. 610 pages. Longmans, Green and Co., New York, 1941. Price, $25.

This dictionary of applied chemistry has been known to practically every chemist alive today, usually from the time of graduation, for it has gone through three previous editions and has been for decades a standby of the chemical profession. It has been used as a standard encyclopedic work for reference ever since the first volume was produced under the authorship of Jocelyn F. Thorpe, later knighted for his accomplishments, who died on June 10, 1940, and to whose memory this work is perhaps his greatest monument.

Volume V, like its predecessors, is arranged alphabetically by subject, each being treated as occasion warrants by England's leading chemical experts. The more lengthy articles are on Fermentation (50 pages), Fertilizers (25 pages), Fibres (71 pages), Finishing of Fabrics (20 pages), Fireproofing (16 pages), Fluorine (12 pages), Food Preservation and Preservatives (20 pages), Fuel (47 pages), Coal Gas (50 pages), and Glass (52 pages). It should be available to all chemists as a reference work, since it will bring them more closely in touch with the present status of applied chemistry and with its literature. The work is invaluable. Charles L. Parsons.

[Longmans, Green and Co., 55 Fifth Ave., New York, N. Y., have published a 19-page abridged index to Volumes I to V of the new edition of Thorpe's Dictionary of Applied Chemistry. This index is available at $1.00.]

INDEX TO A.S.T.M. STANDARDS. Issued by the American Society for Testing Materials, 260 So. Broad St., Philadelphia, Penna. 6 x 9 in. 196 pp. No Charge.

In addition to being essential to the use of the A.S.T.M.'s Book of Standards and its two supplements for 1940 and 1941, this index is also of particular service to those who wish to determine whether the Society has issued standard specifications, test-methods, or definitions covering a particular engineering material or subject. A list is given of the 1043 specifications and tests in numeric sequence of their serial designations. All items in the index are listed under appropriate key-words according to the subjects they cover. [From *The Rubber Age* of New York.]

DU PONT—ONE HUNDRED AND FORTY YEARS. William S. Dutton. Published by Charles Scribner's Sons, 597 Fifth Ave., New York, N. Y. 1942. Cloth, 9½ by 6¼ inches, 396 pages. Indexed. Price $3.

Romance, tragedy, bravery, and humor fill the pages of this exciting, but never sensational biography of a business and the men who fostered its growth from the year 1802 when Eleuthère Irénée du Pont de Nemours established a small gun-powder factory near Wilmington, Del. A number of du Pont associates helped to collect the material from which the author has skillfully woven an account of the ingenuity and ability of many men who contributed in divers ways to the development of a long list of products important in war and peace. Following the detailed story of the company's expansion in the production of explosives, Mr. Dutton describes the diversification of interests in the field of synthetic organic chemicals. The resultant discoveries in du Pont laboratories included new dyestuffs, rayon, cellophane, nylon, plastics, synthetic ammonia, industrial alcohol, photographic film, pharmaceuticals, seed disinfectants, lacquers, more than one hundred rubber compounding ingredients, Neoprene, and other things.

A chapter is devoted to Neoprene. Following the methods of German synthesis of acetylene during the World War, du Pont chemists in 1925 began experiments aimed at the production of chemically made rubber. The coöperation of Father Nieuwland, of Notre Dame University, that aided in the isolation and quantity production of vinylacetylene, and the further research steps that successfully resulted in "chloroprene rubber", are related. The early acceptance of Neoprene by rubber processors for a variety of products, notwithstanding its cost was several times that of natural rubber, the commercial development of the synthetic, and the recent expansion program are carefully summarized. [From the *India Rubber World.*]

S. K.—THE RUSSIAN SYNTHETIC RUBBER FROM ALCOHOL

A SURVEY OF THE CHEMISTRY AND TECHNOLOGY OF THE LEBEDEV PROCESS FOR PRODUCING SODIUM-BUTADIENE POLYMERS

ANSELM TALALAY

THE SPONGE RUBBER PRODUCTS CO., DERBY, CONN.

and

LEON TALALAY

THE CONVERSE RUBBER COMPANY, MALDEN, MASS.

INTRODUCTION

The question of producing synthetic rubber industrially was raised in Russia as early as 1918, and was fostered principally by the quest of the U.S.S.R. for economic independence. Having recognized that 1,3-butadiene is one of the simplest organic compounds capable of being polymerized to a rubberlike substance, the Russian Government provided funds for research in two directions[1]:

(1) To investigate the possibility of obtaining butadiene from a mixture of ethyl alcohol and acetaldehyde, according to the method suggested by Ostromislensky in 1915, for which purpose a pilot plant was erected in Moscow at the Bogatyr Rubber Company.

(2) To continue work started in 1915 by B. V. Buizov in the laboratory of the Leningrad Treugolnik Rubber Plant, using petroleum products as a source of butadiene.

By 1922 the Moscow plant had proved that Ostromislensky's process had no industrial future, for it yielded only 5 to 6 per cent of butadiene instead of the 15 to 18 per cent originally expected. The experimental station operated by Buizov had likewise met with little success by 1925.

Early in 1926, therefore, the Superior Economic Council of the U.S.S.R. announced an open competition for the best industrial method of producing synthetic rubber, setting January 1, 1928 as the deadline. The qualifying conditions were rather exacting. They specified that the synthetic rubber should be neither inferior in quality to, nor substantially different in price from, natural rubber. Aside from a detailed description of the process and a two-kilogram sample of the synthetic product, the competition called for plans of a complete factory layout for its manufacture.

The method submitted by S. V. Lebedev and his collaborators was awarded the prize. Basically, the process comprises the following three stages:

1. Ethyl alcohol is subjected to simultaneous catalytic dehydration and dehydrogenation, resulting in the formation of butadiene.

$$2CH_3CH_2OH \longrightarrow CH_2:CHCH:CH_2 + 2H_2O + H_2$$

2. The butadiene is isolated and purified.

3. The butadiene is polymerized with metallic sodium according to the method of Matthews and Strange.

Lebedev claimed a butadiene yield of 20 per cent, based on the ethyl alcohol consumed. (The theoretical maximum according to the equation is 58.7 per cent.) Early in 1928 a commission checked his claim and confirmed it, finding that alcohol could be converted into butadiene with a yield of 22 per cent.

A pilot factory (Experimental Station S.K.-B.) was completed in 1930, and the first batch of synthetic rubber was produced in January 1931. By the middle of that year the construction of three plants, each of an ultimate capacity of 10,000 tons of synthetic rubber per year was under way. Completed in record time, the first plant (S.K. 1), located in Jaroslawl, began operations in July 1932, and was followed in September by a second one (S.K. 2) in Voronezh. By 1933 two more plants were in operation (S.K. 3 in Ephremov and S.K. 4 in Kazan).

In 1934 11,000 tons, and in 1935 better than 20,000 tons of sodium-butadiene polymer were produced[2]. The second "five-year plan" called for an annual production of 90,000 tons by the end of 1937. It has been claimed that the cumulative quotas set for the plan were actually exceeded[3]. In addition, this synthetic rubber was to be supplemented by another 20,000 tons of rubber per year from domestically grown shrubs. The home-grown rubber production, however, fell short of the original expectation.

The third "five-year plan" (1938 through 1942) called for the construction of an additional twelve to fifteen decentralized plants, some of them, however of smaller capacity than the initial plants. The war probably cut short this expansion program.

The rapid adoption of synthetic rubber by the Russian rubber industry is reflected in the following statistics[4]:

Year	Percentage of synthetic rubber of the total new rubber used
1932	0
1933	4.7
1934	18.5
1935	40.6
1936	54.1
1937[a]	73.0

[a] Estimated from incomplete returns.

The consistent technological improvements and the increased mastery of the process are evidenced by the steady rise in yield of butadiene calculated on the absolute alcohol consumed[5], more markedly so, since the introduction of a new catalyst in 1939.

		Percentage yield of butadiene (based on absolute alcohol used)	Percentage efficiency of the catalytic process
Claimed and verified in 1928		20–22	34–37.5
Average actual figures for all plants in operation	In March 1935	23.5[6]	40
	In 1938	32.5[7]	56
	In 1939	36.3[7]	62
For the last months of 1939		40–41[7]	70

Throughout 1939 the expenditure of alcohol (calculated as absolute alcohol) was 2.806 tons per ton of finished synthetic rubber, and only 6.34 per cent of

the butadiene formed during the catalytic reaction was lost in subsequent operations, *i. e.*, not polymerized to synthetic rubber. The improved technology is likewise reflected in the reduction of the idle time (see below) of the catalytic chambers from 50 per cent in 1934 to 25-30 per cent in 1937, and in the speeding up of the polymerization cycle from 7 or 10 days to 2.1 or 2.7 days over the same period[8].

In 1933 it was estimated[9] that a synthetic rubber plant, operating at its full capacity of 10,000 tons a year, would have an hourly requirement of 3000 kw.-hrs. of electric power, 70 tons of steam, and 1800 cubic meters of cooling water; and would produce *inter alia* an hourly 2,000,000 calories of refrigeration and 7,000,000 calories of heat. Substantial economies have been effected since that date. Thus, to produce a ton of synthetic rubber only one-fifth of the electric power was required in 1937-1938, compared to 1934, one-quarter of the steam, one-half of the heat calories, one-tenth of the calories of refrigeration, and one-third of the cooling water[8]. Each such factory could supply 3000-3500 tons of acetaldehyde, 1500-2000 tons of ethyl ether, and some 2500-3000 tons of higher alcohols each year as by-products.

This article is confined mainly to a consideration of the catalytic process of converting alcohol to butadiene. The conditions affecting the process and the resulting byproducts will be discussed. With regard to the polymerization process, it should be mentioned here that the monomeric raw material subjected to polymerization is a mixture of 77-80 per cent of butadiene, 15-20 per cent of 2-butene[10], and approximately 3 per cent of substances boiling above 0° C, including not more than 0.1 per cent of acetaldehyde. Before polymerization, the mixture is stored in refrigerated tanks. The sodium used amounts to about 0.5 per cent of the synthetic rubber produced.

Until 1935, polymerization was carried out exclusively in jacketed, totally enclosed vessels, under pressure and at an average temperature of 50° C, using immersed, sodium-covered, paraffin wax protected steel rods (socalled combs[11]). In view of the exothermic nature of the reaction (325 calories per gram of butadiene), the speed of reaction and the heat exchange have to be closely controlled. This makes the polymerization a lengthy process.

Since 1935, an alternative (the socalled rodless) method has been added and introduced on a large scale. In this process, polymerization takes place in a gaseous instead of liquid state (as far as can be judged from the scanty disclosures on the subject). The polymer produced in the gaseous state is less plastic, and is considered to be of superior quality and of greater uniformity than that formed in the liquid state.

The product is freed of the 2-butene which it contains after polymerization by a process of vacuum-kneading[12]; simultaneously 0.5-1 per cent of antioxidant, such as aldol-α-naphthylamine, is added.

The final step is refining. This is virtually a necessity because polymerization does not proceed entirely uniformly, and gives rise to overpolymerized strands, which have to be broken up and dispersed or removed. Ordinarily no attempt is made to wash out the sodium.

Russian synthetic sodium-butadiene rubber (S.K.) is not a copolymer, and is structurally akin to German Zahlenbuna (Buna-85 and Buna-115) rubbers. The Karrer plasticities of its various grades range from 0.3 to 0.7, depending on the conditions chosen for its polymerization. Some grades of S.K. therefore require less electric power for processing than does natural rubber.

Like all butadiene polymers, a pure-gum stock of S.K. exhibits very poor mechanical properties, and obtains its "nerve" and strength only after reenforcement with active fillers and after vulcanization. A compound containing 75 to 80 parts of gas black approaches a tensile strength of 3000 lbs. per sq. in., and an elongation at rupture in excess of 600 per cent. A comparison of the basic mechanical properties of a typical S.K. compound[13] with crude rubber[14], German Buna-S (a styrene copolymer)[14] and American Perbunan (an acrylonitrile copolymer)[14] compounds, with progressively increased loadings of carbon black, is presented in Figures 1, 2 and 3.

S.K. is not oil-resistant, although only approximately one-half of its weight is soluble in benzene. It resists oxidation to a remarkable extent[15]. Heating and mechanical working (milling) have practically no effect on its plasticity[16].

Like other butadiene polymers or co-polymers, S.K. synthetic rubber lacks sufficient "building tack", and considerable effort has been expended by Russian technologists to remedy this[17], one of the more successful ways being the combined use of phenylhydrazine and a softener, such as rosin.

This is of particular importance in the case of "built-up" articles, such as rubber footwear. Success has been achieved by a number of expedients, *e.g.*, by reducing the number of parts in a shoe, and the extensive use of shaped diaphragm presses.

The performance of articles made from Russian S.K. rubber in actual usage, *e.g.* tires cannot be conclusively judged without bearing in mind that a number of factors are *a priori* operating against it. Russian carbon blacks are inferior to American brands, and as is well known, the mechanical properties of all butadiene polymers are extremely sensitive to the quality of the carbon black used. Russian tire cord is inferior, and the design of Russian tires is, or at least two years ago was, by admission, lagging behind American tire designs and constructions of the day. Accordingly, the only comparison that can be made is between Russian tires made from 100 per cent S.K. rubber with Russian tires made under identical conditions from 100 per cent natural rubber. We are informed that, in actual road service, the mileage performance of all-synthetic tires lags on the average only some 15 per cent behind natural rubber tires.

THE CHEMISTRY OF THE LEBEDEV PROCESS[18]

The formation of butadiene from ethyl alcohol was first observed by Ipatieff[19]. By passing alcohol vapors over finely divided aluminum at 580°-680° C, Ipatieff obtained fractional percentages of butadiene. In view of the high temperature required for the reaction and the low yield of butadiene obtained, this case must be regarded as a pyrolysis of alcohol, rather than a synthesis of butadiene from alcohol.

Since acetaldehyde is a derivative of ethyl alcohol, Ostromislensky's method of making butadiene by the action of aluminum oxide on a mixture of acetaldehyde and alcohol might possibly be regarded as a synthesis of butadiene from ethyl alcohol.

The only direct method, however, is the Lebedev process. It was first made known in British patent 331,482 (issued June 30, 1930; applied for January 30, 1929) which claims:

1. A method of manufacturing diolefins, consisting of heating methyl, ethyl or propyl alcohol, or mixtures thereof, with a mixture containing a catalyst cap-

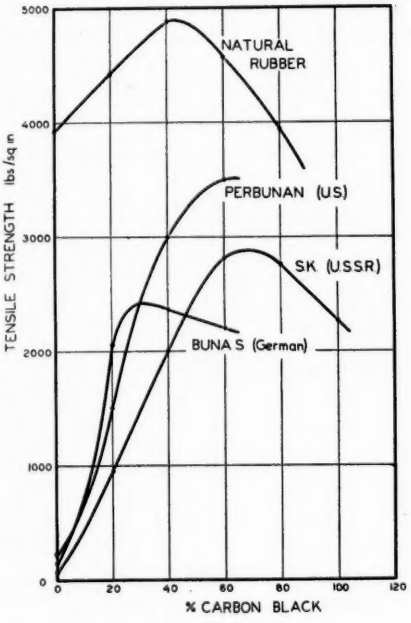


FIG. 1

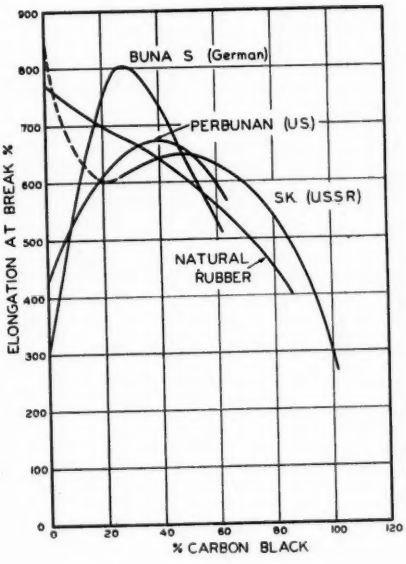


FIG. 2

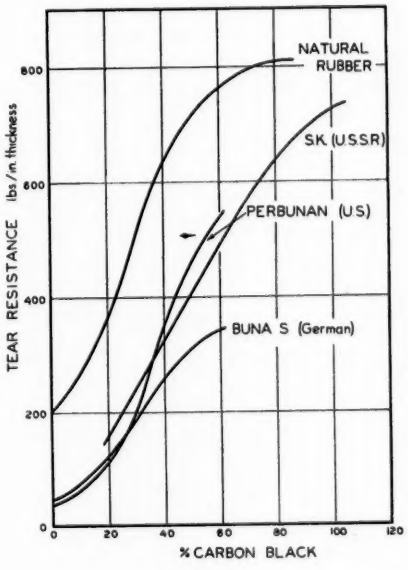


FIG. 3

able of provoking the splitting-off of hydrogen, and a catalyst capable of provoking the splitting-off of water.

2. A method of making diolefins, as in claim 1, consisting of the use of reduced pressures and rapid cooling of the products of the reaction.

3. A method of making butadiene as in claims 1 and 2, consisting of heating ethyl alcohol with a mixture of aluminum oxide and zinc oxide.

The above information was later extended in Russian patent 24,393 (November 24, 1931) which mentions that uranium oxide is a catalyst capable of simultaneously splitting-off water and hydrogen from alcohols, and that mixtures of hydrosilicates or oxides of aluminum with oxides or salts of manganese, etc., also catalyze the reactions of dehydration and dehydrogenation of alcohols.

As already stated, the process is based on the overall reaction:

$$2CH_3CH_2OH \longrightarrow 2H_2O + H_2 + CH_2{:}CHCH{:}CH_2$$

When proceeding ideally, this process should yield for every 100 parts of alcohol:

Butadiene	58.7 per cent
Hydrogen	2.2 per cent
Water	39.1 per cent

The practical yield, however, lags behind the ideal due to the formation of numerous byproducts. The variety of byproducts formed in the catalytic reaction is an indication that the process taking place at the binary catalyst is of a much more complex nature than indicated by the equation given above.

The presence of a dehydrating component in the catalyst, effecting a water-ethylene cleavage, and of a dehydrogenating component, producing primarily a hydrogen-acetaldehyde decomposition, explains the formation of appreciable quantities of ethylene and acetaldehyde as byproducts.

The ethylene and acetaldehyde as such cannot, however, be regarded as the "building" components of butadiene itself, since, in experiments in which a mixture of ethylene and acetaldehyde was passed over the compound catalyst, only negligible yields of butadiene were obtained.

The following explanation of the reaction has been advanced by Lebedev.

As a result of the two independent catalytic processes, the following free radicals (fragments) are formed at the surface of the catalyst:

$$CH_3CH_2OH \longrightarrow H_2O + [-CH_2CH_2-] \quad (1)$$

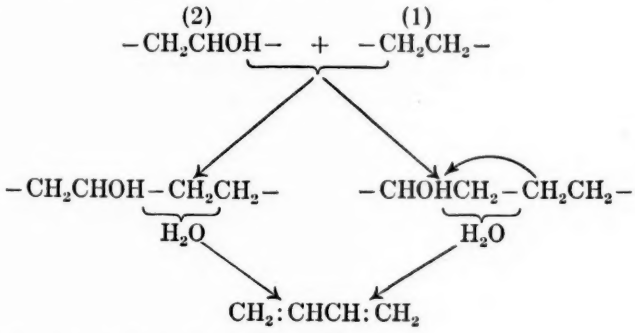
$$CH_3CH_2OH \longrightarrow H_2 + [-CH_2CHOH-] \quad (2)$$

The subsequent behavior of the fragments of type (1), and of type (2), adsorbed on the surface of the catalyst, will depend largely on such factors as the composition of the catalyst, the condition of its surface, the duration of their sojourn on the surface of the catalyst, the concentrations of such fragments and of hydrogen present, the temperature conditions, etc.

Ethylene and acetaldehyde are formed by rearrangement of fragments of type (1) and type (2), respectively, the latter having passed through an enolic stage.

Taking into consideration the various conditions under which the catalytic process is operated (400-450° C, and 2-10 seconds' sojourn in the contact chamber at atmospheric pressure), Lebedev comes to the conclusion that the formation

of butadiene from fragments of type (1) and (2) proceeds in the following manner:



Either of the two paths indicated is possible.

Combination of fragments (1) and (2) seems to take precedence over the formation of products from combination of fragments (1) + (1) and (2) + (2), which accounts for the high yield of butadiene.

The probable mechanism of the formation of six of the major products of the catalytic reaction is summarized in Table I. Explanations have been advanced for the formation of more than twenty byproducts.

Ethers are formed by the dehydrating component of the catalyst by a reaction entirely independent of the formation of butadiene. In practice, however, the temperature at which the process is operated is too high for good yields of ethers, which have been found to be 2-5 per cent of ethyl ether and 0.05-0.1 per cent of ethylbutyl ether.

It is evident that the various main and byproducts, present as the result of the catalytic reaction, have probably been formed in a variety of ways. Butadiene, for instance, may have been formed in at least three or four different ways.

Table II summarizes the twenty major substances identified, and the quantities present, as of time of publication in 1934 of Lebedev's original work. Subsequent improvements in the process and catalyst have changed the percentage composition considerably, and the yield of butadiene obtained is much higher (See statistics above).

THE TECHNOLOGY OF THE PROCESS

The various stages in the operation of the process are presented diagramatically in Figure 4. This flowsheet[20] shows also where the major byproducts of the process are separated.

Alcohol vapors, preheated to the required temperature, pass through the catalytic chamber, which contains a loose mass of the compound catalyst. The product of this catalytic decomposition is a mixture of vapors and gases. These are passed through a condenser system, which permits the gases and vapors of the more volatile liquids to pass on, but condenses any liquids with higher boiling points. The condensate contains considerable quantities of the by-products, which are separated by means of fractional distillation. At this stage also, the unconverted alcohol is separated and returned to the catalytic chamber, via the preheater. The butadiene remains in the gaseous phase, and is extracted on scrubbers, and is irrigated with kerosene, in which it is soluble, along with the gaseous 2-butene and some vapors of volatile liquids.

TABLE I

Product	Percentage	Probable mechanism of formation	Fragments
Ethylene	5–8	$-CH_2CH_2- \rightarrow CH_2:CH_2$	(1)
Acetaldehyde	2.5–5	$-CH_2CHOH- \rightarrow CH_3-CHO$	(2)
Ethane and other saturated compounds	0.4–0.6	$(CH_3CH_2)_2O \rightarrow CH_3CHO+CH_3CH_3$ Ethane is apparently formed by decomposition of ethyl ether rather than from the fragments.	
2-Butene	3–4	$\overset{1}{-CH_2}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{CH_2}-$ By the migration of one hydrogen atom from 2 to 4, 1-butene is formed, which in turn, under the action of the water removing component of the catalyst isomerizes practically completely to 2-butene.	(1)+(1)
1,3-Butadiene	20–25	$\overset{1}{-CHOH}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{CH_2}- \rightarrow$ $CH_2:CHCH:CH_2+H_2O$ By way of splitting-off water and migration of one hydrogen atom from 3 to 1. The complex (1)+(2) on different orientation of the fragments, *i.e.*: $\overset{1}{-CH_2}-\overset{2}{CHOH}-\overset{3}{CH_2}-\overset{4}{CH_2}-$ splitting off water and subsequent stabilization of the molecule leads to butadiene also. This is evidently the simplest way of forming butadiene.	(1)+(2)
Butyl alcohol	2–4	By adding hydrogen to the free valencies of the complex (1)+(2). $-CHOH-CH_2-CH_2-CH_2+2H$ $\rightarrow CH_2OH-CH_2-CH_2-CH_3$ which may lose water and, on isomerization, give rise to 2-butene. $CH_3CH:CHCH_3$ Complex (2)+(2) may lead to aldol, crotonaldehyde, butylene glycol, etc.	

Gas not absorbed in the scrubbers is permitted to escape into the atmosphere. It consists mainly of hydrogen and ethylene. The gas retained by the kerosene is driven off, is washed to extract further quantities of ether and acetaldehyde, and is then subjected to rectification.

Butadiene separated in this way contains 15-20 per cent by weight of 2-butene.

The wash-water and the residue of rectification are each distilled to separate further byproducts, as shown in the flowsheet.

TABLE II

	Percentage
Hydrogen	1.3–1.6
Carbon oxides	0.2–0.5
HYDROCARBONS	
Methane and other saturated compounds	0.4–0.6
Ethylene	5–8
2-Butene	3–4
1,3-Butadiene	20–25
2-Pentene	0.5–0.7
1,3-Pentadiene	0.5–0.7
2-Hexene	0.4–0.5
2,4-Hexadiene	0.6–0.8
Toluene	0.1–0.2
p-Xylene	0.5–0.7
Dimer of butadiene (1-vinyl-3-cyclohexene)	approx. 0.05
SIMPLE ETHERS	
Ethyl ether	2–5
Ethylbutyl ether	0.05–0.1
ALCOHOLS	
n-Butyl alcohol	2–4
Crotonyl alcohol	0.5–1
Amyl alcohol	approx. 0.1
n-Hexyl alcohol	0.5–0.8
Unsaturated *n*-hexyl alcohol	0 05–0.1
n-Octyl alcohol	approx. 0.3
CARBONYL COMPOUNDS	
Acetaldehyde	2.5–5
n-Butyraldehyde	0.1–0.2
Crotonaldehyde	approx. 0.05
Acetone	0.3–0.5
Methylethyl ketone	0.1–0.2

The butadiene-butene mixture is polymerized with sodium. The crude polymer is subjected to kneading under vacuum to remove the 2-butene, which does not polymerize. An antioxidant is added during the kneading operation, and the polymerized mass is finally passed through refining mills, to yield the finished product.

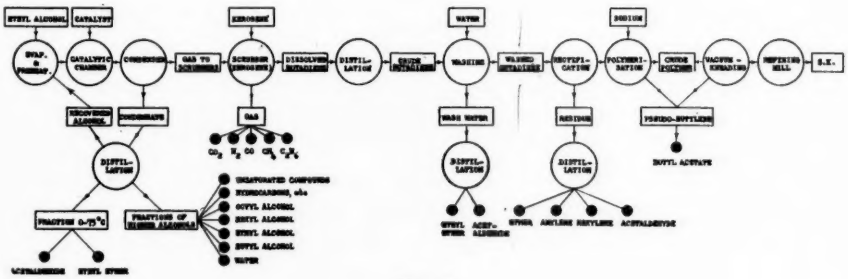


FIG. 4

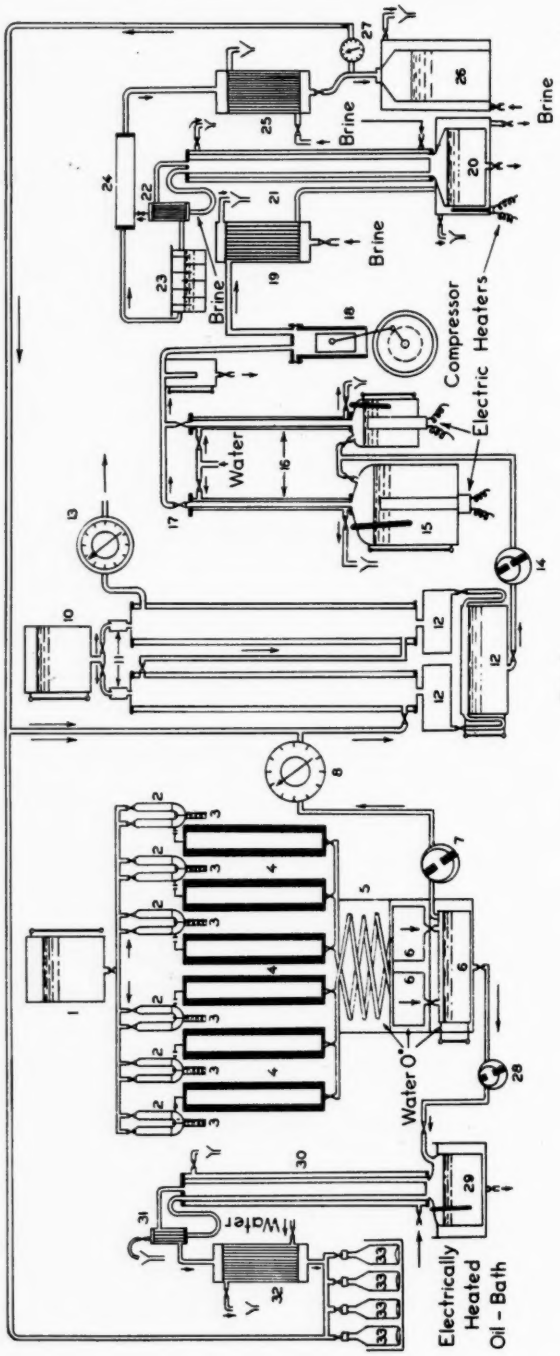

Brine
Brine
Brine
Brine
Compressor
Electric Heaters
Water
Water
Water
Electrically
Heated
Oil - Bath

Fig. 5

A LABORATORY (PILOT) INSTALLATION

A complete pilot plant, capable of processing 3-6 liters of alcohol per hour, has been described by Lebedev, Voljinsky *et al*[23]. With this installation (shown in Figure 5) most of the data for the design and construction of large-scale plants were obtained.

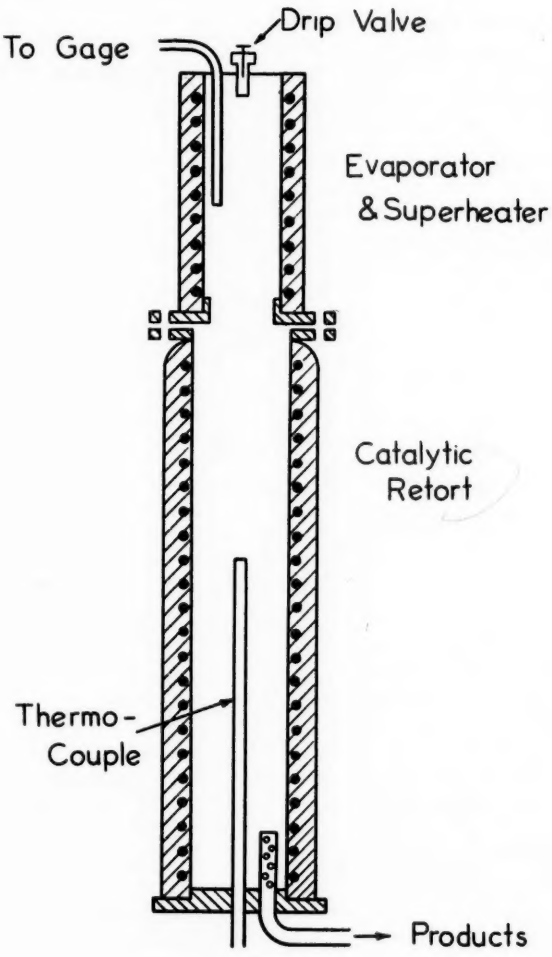


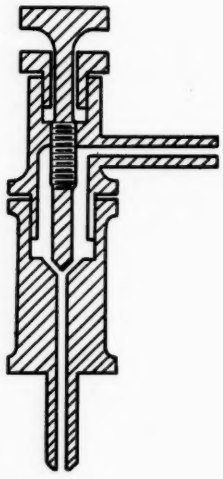
FIG. 6

The installation consists of six catalytic chambers[30] (retorts) (4), one of which is shown in greater detail in Figure 6. Each retort is 1 meter long and 10 cm. in diameter, and has two end flanges. Each top flange is connected to an alcohol evaporator and superheater (3). The bottom flanges are welded on and contain a well, for the purpose of introducing a thermocouple. A perforated tube, by means of which the products of the catalytic reaction are withdrawn, protrudes through the lower flange.

The evaporator consists of a copper tube filled with copper rings. The alcohol is introduced through a drip valve (Figure 7) at the top of the tube, which also has a connection for a pressure gauge.

Both superheater and contact chambers are electrically heated by a single winding of chrome-nickel wire. The chamber is heat-insulated by means of asbestos, containing air spaces. Each retort is both heated and controlled individually.

As can be seen from Figure 5, the alcohol, entering from a pressure tower (1), passes through a distributing manifold to six glass measuring devices (2). From these it is delivered through drip-valves to the evaporators and superheaters (3). Having reached a temperature of 400-425° C, the alcohol enters the contact chambers (4) filled with the catalyst.



Drip Valve

FIG. 7

The gaseous and liquid products of the reaction pass through the cooler (5), which consists of a coiled copper tube. The cooled products are passed into the receivers (6) which can be interconnected. The cooler (5) and receivers (6) are all placed inside a common bath of icewater.

Some of the gaseous products remain dissolved in the condensate; the majority, however, are removed through the rotary exhauster (7), which operates in a vacuum between 30 and 50 mm. of mercury. The gases are pumped through the gasometer (8) to the scrubbers.

The two scrubbers are made of iron pipe. They are filled with coke and are irrigated (sprayed) from a pressure feed tank (10) with turpentine or other absorbent medium, capable of dissolving butadiene, 2-butene and other gases.

One liter of turpentine is used for every 20-30 liters of gas, *i.e.*, for every 70-80 grams of alcohol processed. The turpentine is then collected in three receivers (12).

The gases pass in turn through the two scrubbers, and enter a gas tank through

the gasometer (13). The gases are analyzed every 4 hours. The following is the result of a typical analysis:

Components of gas	Composition (percentage by volume) Before scrubbers	After scrubbers
Carbon dioxide	1–2.5	1.5–3
Unsaturated compounds	45–55	25–35
Air (by oxygen)	3–4	5 approx.
Carbon monoxide	0.5–1	1–1.5
Hydrogen	40 approx.	53–63
Saturated hydrocarbons	3 approx.	2.5–3
Butadiene per liter of gas	0.5 grams	0.050–0.048 grams

It is evident that 90-92 per cent of the butadiene produced is absorbed by the turpentine. The turpentine with the butadiene absorbed in it is pumped into two copper stills (15). These are provided with electric heating elements for raising the temperature of the stills. Butadiene and the accompanying 2-butene begin to boil over at 30-35° C, the greater portion is liberated between 100 and 130° C, and the final amounts of gas escape at 140-150° C. This latter temperature is maintained for at least 15-30 minutes before the evaporation process can be considered complete. To prevent turpentine vapors from passing over into the receiver (20), the gases pass through water-coolers (16).

At times the reciprocating compressor (18) is used, reducing the pressure to 400 mm. of mercury, in which case the maximum temperature at which the last traces of butadiene are liberated is reduced to 110-130° C.

The mixture of gases, after passing through cooler (19), is further cooled to −20° C with brine solution. The condensed gas is passed on to the receiver (20), which is constructed to withstand a pressure of 10 atmospheres. The capacity of this receiver is 25 liters, and is chosen to be slightly in excess of the production of crude butadiene in 24 hours (15-17 liters). By using the compressor (18) and increasing the pressure in the receiver (20) to 3 or 4 atmospheres, it is possible to cool with cold water alone instead of with brine solution.

The crude butadiene mixture contains 82 per cent of fractions boiling below 4° C and about 18 per cent of fractions boiling above 4° C. The fractions boiling below 4° C contain the butadiene, the 2-butene, etc. To separate these, the crude butadiene is rectified by using the receiver (20) as a still. This is done by substituting ordinary water for the brine solution in the jacket, and immersing a heating element therein. Working at atmospheric pressure, the water in the jacket is heated to 25-30° C.

From the still (20), butadiene and 2-butene are passed through the jacketed column (21), which is filled with coke lumps. From there on they are led to the dephlegmator (22), and then are passed through a row of 3-4 washers (23), which are filled with a 50 per cent alkali solution. This washing process removes final traces of acetaldehyde, which would interfere with the polymerization process.

After washing, the gases are dried by passing them through an iron tube (24) containing calcium chloride. They are then cooled in the cooler (25), which is of the same construction and type as cooler (19), and finally are passed into a receiver (26), which is connected to a reducing valve (27).

When the rectification is carried out at atmospheric pressure, the apparatus (21), (22) and (25) is cooled with brine solution, in such a way that the temperature in the dephlegmator (22) at the end of the rectification does not ex-

ceed 2° C, while the cooler (25) and receiver (26) are cooled to −20° C. If the rectification is carried out at an increased pressure, the dephlegmator can be water-cooled. In this case, the cooler (25) and the receiver (26) are cooled with ice water.

The crude butadiene normally contains some dissolved permanent gases, which are the first to escape during the process of rectification, and carry with them a certain amount of butadiene. They are, therefore, passed out through the reducing valve (27), are returned to gas-line ahead of the scrubbers, and are once again passed through the scrubbers, together with the crude gas.

The liquid reaction products of the catalytic decomposition which have been collected in the receivers (6) (see above) are pumped into another receiver (29), placed in an electrically heated oil-bath. They are evaporated through column (30), and pass through a dephlegmator (31) and then through cooler (32), which is water-cooled. As already stated, some of the butadiene has been retained in a dissolved state in the liquid reaction products. When the latter are fractionally distilled, the dissolved gases (mostly butadiene) are driven off first, and are led by means of a special line to a junction point ahead of the scrubbers. The liquid products are gathered in water-cooled receivers (33), and are stored there for further fractional distillation to obtain the various byproducts.

The rectified butadiene stored in receiver (26) is taken away to the polymerization vats, and there polymerized to crude S.K. synthetic rubber.

FACTORS INFLUENCING THE PROCESS

As outlined above, a great number of variables in the catalytic process have a profound effect on the yield of butadiene.

1. Composition of Catalyst [22]

The catalyst is a mechanical mixture of two components: (1)a dehydrogenating agent, which promotes the hydrogen-aldehyde decomposition, and (2)a dehydrating agent, which catalyzes the water-ethylene cleavage.

The relative proportions of the two components (1) and (2) referred to as A and B, respectively, in Figure 8, were varied and the products were analyzed. The experiment was carried out in a catalytic chamber of the pilot plant, and the temperature was maintained at 435-445° C.

The results are shown in Table III. As will be observed from the table, the dehydration reaction catalyzed by component (2) proceeds more easily (more efficiently) than the reaction promoted by component (1) (splitting of alcohol into hydrogen and aldehyde). Consequently there is a deficiency of aldehyde and hydrogen when component (1) alone is used.

From the point of view of maximum butadiene output, the optimum composition of the catalyst corresponds to a mixture of approximately 75 per cent of component (1) and 25 per cent component (2).

Figure 8, which represents graphically the last five columns of Table III, shows clearly that there is a close relationship between the maximum yield of butadiene and properly balanced yields of aldehyde and ethylene.

2. Preparation of Catalyst [23]

In view of the fact that the two catalytic reactions proceed simultaneously and in close proximity, the two catalysts must be mixed intimately. This is achieved by grinding the individual components in porcelain ball mills, mixing,

TABLE III

COMPOSITION OF CATALYST

Composition of catalyst ratio of (1) to (2)	Quantity (R.) of alcohol (87° C) passed	Alcohol (87° C) returned (percentage)	Alcohol used (87° C) (percentage)	Obtained		Composition of gas (percentage by volume)					Butadiene content per liter of gas (R.)	Yield of products expressed as percentage by weight of absolute alcohol				
				Liquid condensate (R.)	Gas (R.)	C_nH_{2n}	H_2	CO	CO_2	CH_4		Ethylene	Ether	Aldehyde	Hydrogen	Butadiene
100 : 0	2800	68.4	31.6	2650	252	20.0	66.0	4.1	6.35	1.58	0.18	2.25	4.4	9.65	1.72	5.8
90 : 10	2850	70.5	29.5	2600	230	35.5	60.3	0.28	3.35	0.0	0.32	3.08	7.13	10.02	1.57	10.1
75 : 25	2800	59.3	40.7	2450	342	43.5	52.6	0.64	1.92	0.42	0.50	5.85	7.25	4.36	1.59	16.6
50 : 50	2750	25.6	74.4	1900	731	84.5	12.8	0.41	0.61	0.40	0.20	31.0	3.52	1.95	0.45	8.2
25 : 75	2900	6.9	93.1	1500	1021	95.5	3.9	0.0	0.91	0.0	0.05	45.3	0.69	1.15	0.14	2.26
10 : 90	2950	6.8	93.2	1550	1060	99.2	0.45	0.0	0.0	0.0	0.023	45.5	0.52	0.89	0.018	0.99
0 : 100	2800	0.0	100.0	1400	1193	98.0	1.73	0.0	0.0	0.0	0.00	55.7	0.00	0.7	0.07	0.00

and homogenizing the mixture in rotating drums for 4-6 hours. An equal weight of water is added to the dry mixture of catalysts and the mixture is made into a heavy paste. The paste is squeezed through a copper sieve, having apertures about 3 mm. in diameter, and the catalyst assumes the shape of little curved cylinders. These are dried for about 4-6 hours at 60°-80° C, in a current of air. (Specific gravity of compound catalyst: 2.96-2.77.)

3. Shape of Catalyst

The shape of the particles of the catalytic mixture and the fineness of subdivision were investigated. The alcohol vapors were preheated to 400°-425° C,

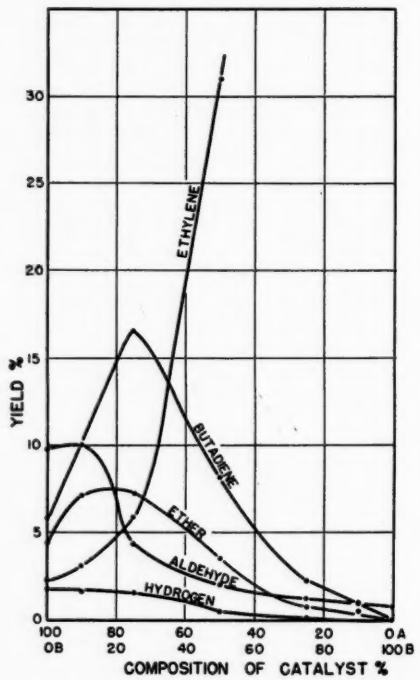


Fig. 8

the temperature of the chamber was maintained at 435°-445° C, and the pressure at 740 mm. of mercury. The alcohol was added at the rate of 11-12 cc. per hour per sq. cm. of cross-section of the contact chamber.

Lebedev[23] and his collaborators found that the loose form of catalyst in the shape of little curved cylinders is superior to the compressed pellet form. The surface area for any given mass of catalyst has a profound effect on the yield of butadiene, as can be seen from Figure 9; the yield improves with greater subdivision[25]. The surface area of the catalyst mentioned above is only the outward geometrical surface. The cylinders are no doubt porous, and the true surface of the catalyst is not known exactly.

Summing up their work on the state of subdivision of the catalyst, the investigators concluded that the most advantageous form of catalyst is a loosely-packed

mass in the shape of little curved cylinders 1-3 mm. in diameter. The use of larger cylinders or compressed pellets lowers the yield of butadiene.

4. Activation of Catalyst [23]

The catalyst is activated by heating it for 10 hours at 500°-550° C, and maintaining a slight current of air. Both temperature and duration of activation are important.

5. Quantity of Catalyst

Smirnov[24] found that the yield of butadiene in a given time, with all other factors constant, is proportional to the quantity of catalyst employed, and is independent of the construction of the catalytic chamber. In a chamber of production size, 90 kg. of catalyst yield 7-10 kg. of butadiene per hour.

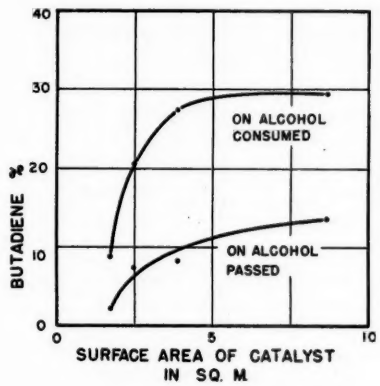


Fig. 9

6. Heat Required for the Reaction

The heat consumption in the various regions of the catalytic chamber was investigated. For this purpose, a chamber 3.5 meters long and of 113 sq. cm. cross-section was used. It was divided into four regions (Nos. 2, 3, 4, and 5), each 75 cm. in length and each filled with the compound catalyst. In addition there was a region 25 cm. long at the top (No. 1) through which the alcohol vapors entered the retort, and which was filled with copper rings, and another region 25 cm. long (No. 6) at the bottom of the chamber, which was left empty. Each one of the regions filled with catalyst could be heated independently by means of an electric heating coil.

The temperature of the alcohol introduced, as well as the temperature of all regions of the catalytic chamber, was maintained at 425°-450° C. Whereas it required only 7 amperes (110 volts) to maintain this temperature in regions 3, 4 and 5, it required 12 amperes for region 2. Thus, almost three times as much heat was used up in region 2, which comes in contact with the alcohol vapors first, as in each of the other regions.

Factory experience has shown[26] that 220 kilocalories are required to decompose 1 kg. of alcohol (85 per cent absolute), preheated to 450° C. In addition

to this, about 328 kilocalories are required to preheat 1 kg. of alcohol from 35° to 450° C, which figure includes the latent heat of evaporation.

7. Preheating of Alcohol

The foregoing discussion indicates that preheating of the alcohol is important. Thus, for a given height of catalytic layer in the chamber, the yield of butadiene dropped from 19.4 to 12.0 per cent when the temperature of the preheated alcohol was lowered from 450° to 300° C. It appears that, in the latter case, a part of the catalyst acts purely as a preheater since, on examination after prolonged contact, the layer of catalyst first encountered by the alcohol vapors was found to be white and uncarbonized.

8. Temperature

In considering the effect of temperature on the yield of the catalytic reaction, a number of factors must be borne in mind:

(a) Staudinger[27] in 1913 found that butadiene is unstable at high temperatures. Elevated temperatures, therefore, although generally activating the catalyst in an endothermic reaction, tend to promote decomposition of the butadiene formed, provided it remains long enough in the high temperature zone (at the catalyst).

(b) Increased temperatures may activate the two individual components of the compound catalyst to different degrees, throwing their action out of balance, and thus create an adverse effect on the yield of butadiene.

(c) Temperature also affects the active life of the catalyst. To illustrate the implications of the above, the following experiments are cited:

1. High temperature decomposition of butadiene.

Pure butadiene was led through a copper tube filled with the catalyst. The tube was 20 cm. long and 2.5 cm. in diameter, and the butadiene was fed through at the rate of 14.5 cc. per sq. cm. per minute. The following results were obtained:

Temperature of chamber (°C)	350-365°	400-415°	450-465°	500-505°
Percentage decrease of C_4H_6 in the escaping gas	9.9	23.8	31.2	69.1

2. Catalytic reaction and temperature.

Experiments for the purpose of studying the temperature effect, ignoring for the time being any deterioration of catalytic activity with time, and maintaining a constant rate of delivery of 10.3-10.4 cc. per sq. cm. per hr. in a chamber one meter long and 75 mm. in diameter, other factors being constant, gave the results shown in table at top of page 421.

The experiment lasted twenty-fours hours in each case.

An increase in temperature activates both the dehydrogenating and dehydrating components of the catalyst. At temperatures above 450° C, however, the activity of the two components of the catalyst seems to get out of balance, so that, in spite of the greater percentage of alcohol decomposed and the larger volume of gas formed, the percentage yield of butadiene falls appreciably.

In practice, the economic operation of the process depends both on a high percentage of butadiene and on a high yield for a given apparatus, *i.e.*, it is desirable that the quantity of alcohol not decomposed should be low.

Temperature of chamber (°C)	360-375°	400-415°	435-445°	460-475°
Quantity of butadiene per liter of gas (g.)	0.24	0.51	0.61	0.50
Gas per kg. of alcohol delivered (liters)	44.5	98.7	232.	261.
Water in percentage of alcohol delivered	17.0	18.0	22.6	38.4
Alcohol returned unused (percentage)	85.0	61.0	36.0	21.2
Content of unsaturated compounds in gas (percentage)	29.8	48.0	50.0	52.0
Aldehyde content in percentage by weight of alcohol delivered	0.7	0.8	1.35	1.86
Hydrogen in gas (percentage by volume)	61.7	67.5	46.5	44.0
Butadiene (percentage based on alcohol decomposed (consumed))	7.5	13.9	23.2	17.7

Smirnov[24], working under actual factory conditions, confirmed the fact that there is no real practical advantage in changing the temperature. His data are summarized in the following table:

Temperature of catalytic reaction (°C)	420°	440°	450°	460°	470°
Yield of butadiene (percentage of absolute alcohol decomposed)	26.0	24.5	25.3	22.4	22.5
Yield of butadiene (percentage of absolute alcohol passed)	9.5	11.1	12.7	12.9	13.7
Productivity of chamber (kg. of butadiene per hour)	6.1	7.5	7.7	7.8	8.2
Alcohol returned undecomposed (percentage)	67.2	59.2	54.8	48.2	45.2

Smirnov confirmed the fact that, within the limits of 420°-450° C, the yield of butadiene, expressed as percentage of alcohol decomposed, changes very little. Above 450° C it falls rapidly, offsetting any possible advantage derived from a lesser return of undecomposed alcohol and fractionally higher yield of butadiene per hour.

A further economic consideration is the fact that increased temperature materially prolongs the time required to reclaim the catalyst[24]. This is convincingly shown by the following table:

Temperature of catalytic reaction (°C)	420°	440°	450°	460°	470°
Average time (hours) required for reclaiming, after catalyst has been used continuously for 11.5 hours	5.5	7.75	9	11.25	12
Time of reclaiming (percentage of time of contact)	47.8	67.2	78.2	98.0	104.3

9. Rate of Alcohol Delivery to Catalytic Chamber

Smirnov[24] investigated also the influence of the rate of alcohol delivery under actual factory conditions. He found that, whereas the change in rate has only a slight effect on the yield with respect to the alcohol decomposed, both the

alcohol returned undecomposed and the productivity of the chamber are affected, as shown in the following table:

Rate of alcohol delivered (kg per chamber per hr)	Time of contact (sec. @ 450° C)	Butadiene in percentage of absolute alcohol		Return of alcohol (percentage undecomposed)	Butadiene productivity (kg per chamber)
		Decomposed	Passed		
41.0	14.1	24.0	13.8	33.0	5.7
63.2	9.1	21.6	11.6	37.4	7.3
68.1	8.5	21.6	11.6	37.4	7.9
98.0	5.9	21.3	10.4	43.2	10.2
101.5	5.7	22.4	9.9	48.8	10.0

On the whole, the rate of delivery of alcohol affects the yield far less than does the temperature.

10. Temperature and Rate of Delivery

At increased temperatures the reaction is activated. A similar effect is had by decreasing the rate at which alcohol is delivered into the chamber. Furthermore, at a rapid rate of delivery the temperature effect is lessened, since alcohol vapors remain in contact with the catalyst for a shorter time. At a higher temperature and a faster rate of delivery, therefore, a normal yield of butadiene should be obtained, and thus it might be possible to increase substantially the productivity of a given contact chamber. This is illustrated by the following experimental series, in which both the temperature and rate of delivery were varied:

Temperature of experiment (°C)	410-415°	435-445°	460-475°
Alcohol delivery (cc. per sq. cm. per hr.)	9.9	10.3	24.4
Butadiene content per liter of gas	0.62	0.61	0.52
Liters of gas per kg. of alcohol delivered	151.	232.	308.
Water in condensate (percentage by weight of alcohol delivered)	12.9	22.6	24.7
Alcohol returned (percentage)	57.9	36.0	24.7
Unsaturated compounds in gas (percentage)	45.0	50.0	45.5
Aldehyde (percentage by weight of alcohol delivered)	0.9	1.35	2.7
Hydrogen content in gas (percentage)	53.0	46.5	48.2
Yield of butadiene (percentage of alcohol consumed)	23.1	23.2	22.3

We see, therefore, that a simultaneous increase in both temperature and rate of alcohol delivery can produce a good yield (22-23 per cent) of butadiene.

One must bear in mind, however, that higher temperatures make the catalyst "tire" (poison it) more rapidly; against this no practical remedy is yet available.

11. Reduction in Pressure

Reduction in pressure in the chamber (up to about 130 mm. Hg) improves the yield of butadiene. Further reduction in pressure, however (beyond 240 mm. Hg), again decreases the yield. In the same fashion, increased pressures (above atmospheric) are unfavorable. One observes a reduced yield of gas and a lower butadiene content of the gas, which jointly lower the yield of butadiene.

12. Poisoning and Reclaiming of Catalyst [23]

From the outset of their work, Lebedev and his collaborators observed a progressive deterioration in the performance of the catalyst. Both the quantity of gas generated and its butadiene content decreased with time. The following table shows this progressive deterioration. The gas was analyzed every two hours.

Hours	Gas generated in 2 hrs. (liters)	Butadiene content per liter (grams)	Unsaturated compounds (percentage)	Condensate obtained in 2 hrs. (grams)	Alcohol returned (percentage)	Butadiene (percentage of absolute alcohol)	
						Delivered	Consumed
2	2615	0.51	45.5	4085	15.8	16.6	21.9
4	2315	0.54	43.0	4455	23.2	16.2	23.5
6	2270	0.52	42.5	4900	25.0	15.2	20.6
8	2290	0.52	42.5	4930	25.2	15.1	22.4
10	2420	0.52	42.0	4390	21.1	16.7	23.4
12	2355	0.52	41.6	5015	26.0	15.7	23.5
14	2065	0.50	41.5	5195	29.8	12.8	20.2
16	1985	0.50	40.2	5340	32.0	12.5	20.4
18	1775	0.49	40.5	5105	34.8	11.3	19.2
20	1600	0.49	40.5	5550	39.6	8.1	16.9

It appears that, after 14-16 hours, the efficiency begins to decrease and, after 19 hours, the yield of butadiene, calculated as percentage of absolute alcohol consumed, has fallen to 16.9 per cent instead of 23 per cent at the outset of the experiment.

The reason for the fatigue of the catalyst is the fact that carbon becomes deposited on its surface, clogs the pores, and thus reduces the available active surface. Furthermore, carbon itself acts as a catalyst, and leads the process in an undesirable direction. Carbon formation is mainly associated with component (2) of the catalyst (water-withdrawing component). Usually 1-2 per cent of carbon by weight of catalyst is formed during a run of 12-16 hours (*i. e.*, 0.16-0.23 per cent per kg of alcohol delivered). Carbon deposits more readily on a fresh catalyst than on a regenerated one.

The catalyst is reclaimed by burning in air the carbon deposited on it. For this purpose, the inflow of alcohol is interrupted, the chamber is blown out with steam, the temperature is brought to 450° C, and air is delivered to the chamber. Since the catalyst, or rather its component (2) (water-withdrawing), is poisoned at temperatures above 600° C, air must be introduced carefully, so that combustion of the carbon causes no overheating of the catalyst. Normally the temperature inside the catalyst is maintained at 520-550° C during regeneration.

Combustion of carbon does not occur simultaneously throughout the mass of the catalyst, but begins in the zone with which air comes into contact first, and then gradually proceeds throughout the mass.

The uneven deposition of carbon makes occasional local overheating inevitable, but this can be overcome by throttling the air stream. In factory operation, regeneration is often carried out with a mixture of air and steam. The progress of regeneration is controlled by determining the carbon dioxide in the escaping air. The time required to regenerate the one meter chamber was 8-10 hours (after 12 hours of contact). Tests have shown that regeneration can be materially accelerated, by supplying air simultaneously to different regions of the chamber.

The regeneration is discontinued as soon as the carbon dioxide content of the escaping gas has fallen below 1 per cent. Further regeneration, to absolute completion, is unnecessary, since the yield of butadiene is just as high as at the beginning.

The working qualities of the regenerated catalyst were ascertained by a series of experiments, consisting, in each case, of 12 hours' time of contact, followed by regeneration at 500-550° C, which was continued until carbon dioxide could no longer be detected in the escaping gas. Up to, and including the tenth consecutive experiment, the yield of butadiene was approximately 20 per cent (on absolute alcohol consumed), it then fell to 16 per cent, and, beginning with the twenty-first consecutive regeneration, it decreased to 14 per cent.

13. Effect of Admixtures to Alcohol

The result of adding various substances to the alcohol before contact was investigated[28], and their effect on the yield of butadiene is shown in Figures 10 and 11.

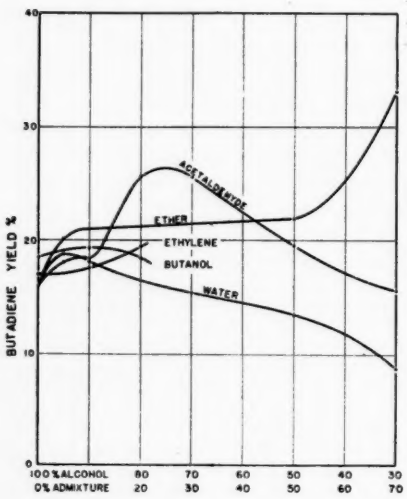


Fig. 10

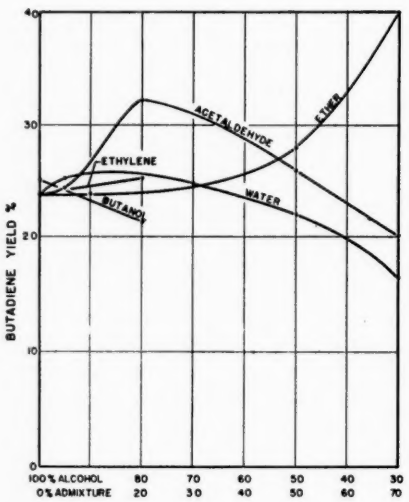


Fig. 11

A study of these curves confirms previous conclusions to the effect that:

(1) Acetaldehyde takes part in the formation of butadiene, although by itself it forms no butadiene (this follows from the curve in both charts).

(2) Ether takes part in the formation of butadiene, but, unlike acetaldehyde, is capable itself of forming butadiene. However, the yield of butadiene obtained from pure ether is smaller than that from pure alcohol.

(3) Ethylene introduced simultaneously with the alcohol evidently plays a considerable part in the formation of butadiene.

(4) Slight dilution with water has practically no effect on the yield of butadiene, as can be seen from the charts. At greater dilution, the yield falls off rapidly.

In practice, crude alcohol (84.6 per cent absolute alcohol by weight) is used, and this gives a yield of butadiene equal to that of rectified alcohol (92.5 per

cent absolute alcohol by weight). According to Sabatier, water is detrimental to the dehydrogenating process. This was confirmed by Lebedev's collaborators, who obtained the following yields, when all other conditions were kept constant:

Percentage by volume of absolute alcohol in the alcohol used	Temperature (°C)	Percentage yield of butadiene (calculated on absolute alcohol consumed)
94.5	440	23.2
94.5	500	17.7
76	440	16.5
76	500	19.3
54	440	15.0
54	500	18.8

A slight improvement is observed when the more dilute alcohol is contacted at higher temperatures.

(5) Butyl alcohol takes no part in the formation of butadiene, and its presence impairs seriously the yield of butadiene.

14. Conclusions

Summarizing the best operating conditions for the catalytic process, we arrive at the following conclusions:

1. The two components (1) and (2) of the catalyst must be intimately mixed in the ratio of 25 per cent of (2) and 75 per cent of (1.) The compound catalyst must be present in a form exposing the maximum possible active surface[25].

2. The alcohol must be evaporated, and fully preheated to 450° C before entering the catalytic chamber. In a plant operating at a capacity of 10,000 tons of S.K. rubber per year, this is accomplished by a single tubular evaporator and superheater. The evaporator is capable of handling approximately 11,000 kg. of alcohol per hour, and consumes 3,610,000 calories per hour, *i.e.*, 328 calories per kg. of alcohol.

3. Alcohol of 85 per cent absolute concentration is used, mostly admixed with partly returning (unused) alcohol of 96 per cent absolute concentration.

4. No substantial advantages can be derived from a change in the temperature of operation outside of the limits of 435-450° C. The time of contact with the catalyst must be maintained at about 10 seconds.

5. For a factory of standard size (10,000 tons per annum), the equipment consists of 12 furnaces, mostly oil-fired, each containing sixteen catalytic chambers, arranged in circular fashion. Each chamber is loaded with 90 kg. of catalyst. Each furnace receives approximately 1100 kg. of alcohol vapors per hour, and is capable of decomposing up to 750 kg. of alcohol vapors in this time, consuming 165,000 calories and producing 170-180 kg. of butadiene per hour. (These are figures based on a maximum yield of 25 per cent, which has been substantially improved.)

6. The catalytic reaction is continued for 11 to 12 hours, when the catalyst must be reclaimed, which is done by blowing it out with a mixture of air and steam at 500-550° C.

7. The contact gases are cooled to approximately 150° C by the incoming fresh alcohol, and then to about 80° C with water.

RUSSIAN WORK ON BUTADIENE DERIVED FROM PETROLEUM AND ITS FRACTIONS [29]

Considerable attention has been focused in the United States and abroad on petroleum products as a cheap source of butadiene. Although the process is apparently not in large-scale operation in Russia, on account of the fact that the alcohol process is the more efficient of the two under conditions of Russian economy, extensive research has been done by Russian investigators on this subject.

It is well known that the thermal decomposition of petroleum yields quantities of butadiene, together with isoprene and other diolefins. Work was done to establish the processing conditions most favorable to the formation of 1,3-butadiene from products of the Russian crude oil industry.

Petroleum products from the Baku region of the Caucasus, known to be rich in naphthenic hydrocarbons such as cyclohexane (b.p. 75° C), methylcyclohexane (b.p. 100° C) and 1,3-dimethylcyclohexane (b.p. 120° C), were used.

TABLE IV

No.	Substance	Density d_{15}	Flash point (°C)	Viscosity @ 20° C	Optimum butadiene (percentage)	Best Temp. (°C)	Optimum flow (cc. per min. per sq. cm. cross-section)
1	Gasoline	0.7495	—	—	11	750	0.48
2	Kerosene	0.8247	—	—	5.22	750	0.46
3	Lubricating oil	0.8862	146	2.54	3.91	735	0.16
							0.24
4	Crude oil	0.8952	42.3	4.68	3.73	750	0.43
5	Mazout	0.9351	152	—	2.55	715	0.36
In addition, the following individual fractions of gasoline were investigated.							
6	77-85 °C	0.7036	—	—	7.50	750	0.45
7	101-103 °C	0.7364	—	—	11.00	750	0.45
8	117 °C	0.7599	—	—	8.37	750	0.45
9	120.6 °C	0.7707	—	—	7.41	750	0.45

In view of the fact[27] that butadiene is unstable at high temperatures, the method involved a short heating and a subsequent rapid cooling (quenching) of the gaseous decomposition products. Neither substantial reduction in pressure nor dilution with inert gases was used, although such procedures are known to increase the yield of butadiene.

Only two conditions were varied, the temperature and the speed of flow of the material through the heated zone of the apparatus (a quartz tube). The products investigated and the results obtained are shown in Table IV.

The boiling characteristics of products 1-4 are given in Figure 12.

The investigators came to the conclusion that:

1. The yield of butadiene obtained as a result of thermal decomposition (pyrolysis) of various petroleum fractions varies within wide limits. Mazout gives the lowest yield (2.5 per cent). The yield is higher for lubricating oils and kerosene and reaches its maximum for gasoline (11 per cent), as can be seen from Figure 13 and Table IV. The various fractions of gasoline again yield varying amounts of butadiene.

2. The optimum temperature of the pyrolysis is higher for the lighter fractions of petroleum than for the heavier ones. For Mazout it is 715° C, for gasoline it is 750° C (see Figure 14).

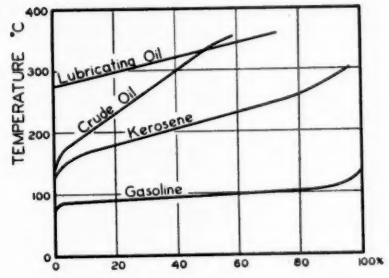


FIG. 12

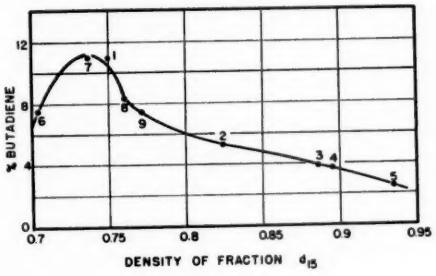


FIG. 13

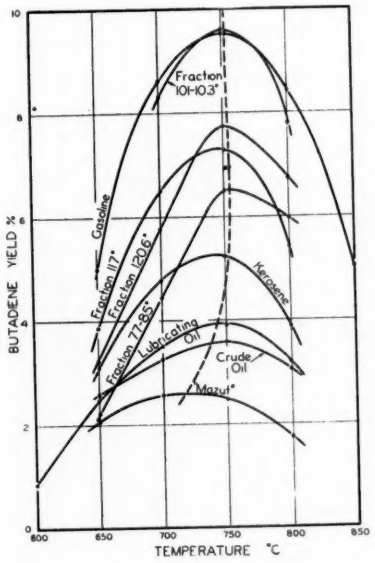


FIG. 14

3. The optimum speed of passage varies only to a small extent from product to product, and is found to be in the region of 0.4-0.5 cc. per min. per sq. cm. of cross-section (see Figure 15).

4. For heavy fractions, the yield declines only slightly when deviating from the ideal conditions; for the light fractions, however, the yield is considerably decreased (see Fgures 14 and 15).

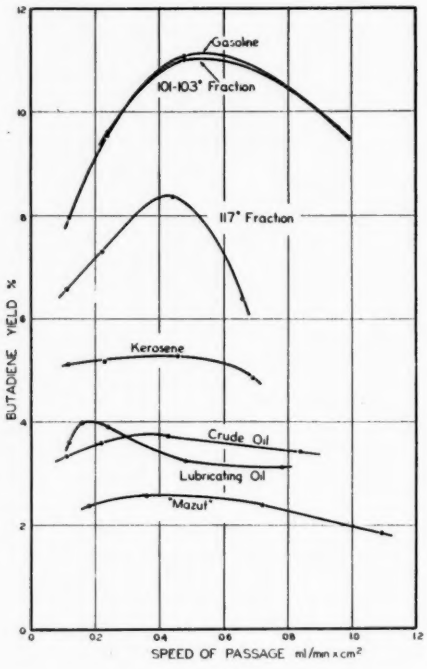


FIG. 15

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[7] Petrenko, *Kauchuk i Rezina* **1940**, Nos. 4-5, p. 1.
[8] Borisovitch, *Kauchuk i Rezina* **1939**, No. 10, p. 5.
[9] Lurie, *Zh. Syntet. Kauchuk* **2**, No. 1, 23 (1933).
[10] Because of the closeness of their boiling points, no attempt is made to separate butadiene and 2-butene. Unlike a number of impurities in butadiene made from petroleum fractions, 2-butene does not interfere in any way with the polymerization process. A chemical procedure for separating butadiene and 2-butene has been described by Freedstein, Tuileneva and Safonov (cf. *Zh. Syntet. Kauchuk* **4**, No. 3, 13 (1935)).
[11] Zavalkov, *Zh. Syntet. Kauchuk* **3**, No. 3, 15 (1934).
[12] Of the various possibilities of utilizing 2-butene, its conversion into butyl alcohol is worthy of note (cf. King, *J. Chem. Soc.* (London) **115**, 1406 (1919)), and his collaborators (cf. S. V. Lebedev, "Zhizn i Trudui", Moscow, **1938**, p. 601), and was found to give a 70-72 per cent yield of butyl alcohol, provided that not over 3-4 per cent of butadiene is present in the 2-butene.
[13] The physical data on S. K. are taken from work by Lebedev and his collaborators (cf. *Trudui Gosudarstvenovo Opuitnovo Zavoda Syntetichekovo Kauchuka Lit. B.* (Leningrad) **3**, 85, 100 (1934).
[14] The data for crude rubber, Buna-S and Perbunan are experimental results obtained by one of the authors (A.T.) of the present paper, and he wishes to express his appreciation to the Advance Solvents and Chemical Corporation (New York) for the facilities afforded him.

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[23] Lebedev, Voljinsky, Krupuishev and collaborators, *Trudui Gosudarstvenovo Opuitnovo Zavoda Syntetícheskovo Kauchuka Lit. B.* (Leningrad) **3**, 16 (1934).
[24] Smirnov, *Zh. Syntet. Kauchuk* **3**, No. 1, 13 (1934).
[25] A limitation to this last condition is the fact that the catalyst may be carried away with the gas if it is of very fine particle size. The gas travels at the rate of 1 meter per second in the chamber, and 16 meters per second in the ducts. This difficulty necessitates the installation of cyclone dust collectors; otherwise, clogging of the coolers and condensers results.
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[28] Lebedev and collaborators, *Zh. Syntet, Kauchuk* **4**, No. 8 (1935); Lebedev, "Zhizn i Trudui", Moscow, **1938**, p. 602.
[29] Lebedev and collaborators, cf. Lebedev, "Zhizn i Trudui", Moscow, **1938**, p. 471.
[30] The retorts can be made of copper, enameled iron, or iron lined with aluminum. The material does not affect the yield significantly. As for the dimensions of the pilot plant (see Figure 5), the capacity of the pressure tower (1) is 10 liters. Each of the two smaller receivers (6) also has a capacity of 10 liters. The capacity of the largest receiver (6) is 48 liters. The scrubbers are 180 cm. high and 15 cm. in diameter. The volume of the feed tank (10) is 42 liters. The volume of each of the smaller receivers (12) is 20 liters; that of the larger is 100 liters. The stills (15) have capacities of 100 and 25 liters, respectively. The coolers (16) are each 1 meter high and 18 mm. in diameter. The cooling surface of the cooler (19) is 600 sq. cm. Each of the dephlegmators (22) and (31) has a cooling surface of 150 sq. cm.

THE KINETICS OF HIGH ELASTICITY IN SYNTHETIC POLYMERS *

R. F. TUCKETT

DEPARTMENT OF COLLOID SCIENCE, THE UNIVERSITY, CAMBRIDGE, ENGLAND

The theory of rubberlike elasticity which is usually associated with the names of Meyer, Mark, and Kuhn[2], deals essentially with the equilibrium magnitude of the strain produced in a rubber by a given stress. In natural rubber this equilibrium value is reached almost at once at room temperatures, but this is not so in other macromolecular assemblies; thus the simple theory would appear to need extension so that the elastic behavior of other high-polymer systems can be fitted into a general framework, which includes rubber as a special case. The work of Alexandrov and Lazurkin[3], who treated the development of a highly elastic strain as a unimolecular rate process, gave considerable insight into a possible method of approach, and this concept has been extended further in terms of the activated complex method by Eley[1], with whose general conclusions we are in substantial agreement. The present work describes a concurrent attempt to connect qualitatively the elastic properties of synthetic polymers with their molecular structure in terms of this general line of attack; their relation to other physical properties of polymers is also brought out.

GENERAL THEORY

Following Alexandrov and Lazurkin[3], the elastic deformation produced in a polymer by a given stress can be divided into two components; one of these (D_{OE}) is always attained instantaneously, and corresponds to a high Young's modulus (10^2-10^4 kg. per sq. mm., according to Kuhn[4])—this is due to chain separation as distinct from chain uncoiling, which is responsible for the other component (D_{HE}). In the present treatment, only the latter highly elastic portion is considered. It corresponds to a very low Young's modulus ($\sim$0.2 kg. per sq. mm.) and hence, when fully developed, is very much larger than D_{OE}. D_{HE} is, however, dependent on time, and can be expressed in the form:

$$D_{HE}(t) = D_{HE}(\infty)\left(1 - e^{-\frac{t}{\tau}}\right)$$

where t is the time of loading; $D_{HE}(\infty)$ is the final equilibrium value of $D_{HE}(t)$, and τ is a characteristic "orientation time". (This should not be confused with a relaxation time in the Maxwell sense.) From this equation, it is seen that the relative magnitudes of t and τ determine whether a given polymer exhibits high elasticity at a given temperature: if $\tau \ll t$, high elasticity is developed at once but the magnitude of the final deformation ($D_{HE}(\infty)$) is not affected by t or τ directly. For $\tau \gg t$, D_{HE} is hardly developed at all, and $D_{OE} \gg D_{HE}(t)$. The effect of molecular size, structure and environment on these factors will now be considered.

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If τ is treated as a unimolecular rate constant, it can be expressed in the form: $\frac{h}{kT}e^{+\frac{\Delta G}{RT}}$, where ΔG is the Gibbs free energy of activation for orientation[5] ($\Delta G=\Delta H-T\Delta S$); as ΔG is the only independent variable for a series of polymers at a given temperature, the absolute magnitude of τ is defined almost entirely by ΔG, which determines the temperature range over which a polymer develops high elasticity. It should be pointed out here that this range may be quite small, owing to the large value of ΔH ($\sim$50-100 kilocalories) but that there is no sharp demarcation between the two regions of high elasticity (corresponding to low Young's modulus) and ordinary energy elasticity (high Young's modulus). We can, however, define an elastic temperature, T_E, at which τ has a fixed value (say 1 sec.), and this is a convenient way of comparing the elastic properties of different polymers. Substances at temperatures where each has the same τ value will be termed isoelastic, and it is often possible to derive isoelastic temperatures from published data although the τ value to which they correspond is not known. If T_E (corresponding to a τ value comparable with an average time of loading) is much less than room temperature, then the polymer under normal conditions can undergo large extensions which are ultimately reversible. This is so for natural rubber, polychloroprene and polyisobutenes. Larger values of ΔG will, however, correspond to high T_E values, and such substances will develop rubberlike properties only at higher temperatures. Table I gives some idea of the range of T_E values for a number of unplasticized polymers. The distinction between synthetic rubbers and ordinary thermoplastic polymers is thus seen to be one of degree rather than of kind. T_E is essentially dependent on τ and if the latter is small enough, T_E corresponding to it is raised considerably. For this reason, a natural rubber can behave as a hard solid if a high frequency variable stress is applied to it.

TABLE I

Polymer unit	T_E °C
Isoprene (rubber)	— 50- — 70
Chloroprene	— 50- — 70
Isobutene	— 50- — 70
Vinyl acetate	+ 35- + 45
Methyl methacrylate	+ 70- + 90
Styrene	+ 70- + 90
Vinyl chloride	+ 100- + 110

THE PHYSICAL INTERPRETATION OF ΔG

In general, the absolute magnitude of ΔG will be some function of the forces between the chains and those between the adjacent units in single chains; on this basis, it is permissible to speculate on the physical meaning of the quasi-thermodynamic concepts outlined above, and especially whether the development of high elasticity as the temperature is raised corresponds to any other physical change in the system. A possible connection comes from the work of Ueberreiter[6], who has measured the volume-temperature relations of a number of polymers: for each system, this can generally be analyzed into two straight lines, with a definite break point (T_F). Ueberreiter considers this to represent the freezing-point of the polymer, corresponding to the transition from a liquid to an unordered structure similar to that found in glasses. Since the solid molecules can move only about fixed positions below T_F, the coefficient

of volumetric expansion will be less than for a liquid, and there will be a discontinuity in the volume-temperature relation. On cooling a substance through to the glasslike stage, two effects will contribute to this break—one volume change occurs instantaneously at the cooling temperature; the other is time-dependent, and proceeds rapidly only at elevated temperatures. According to Ueberreiter, the instantaneous change is due to an alteration in the interchain distance, which does not affect their relative geometrical position; the latter volume effect is caused by a definite relative positional change. Now, this distinction is very similar to that between ordinary and high elasticity in polymers as developed by Alexandrov and Lazurkin, and it seems that both sets of phenomena might be ascribed to the same basic causes; this is made more plausible by the fact that in the cases where a comparison can be made, Ueberreiter's T_F values are very close to the temperature ranges over which high elasticity develops[7].

Hence it appears worthwhile to identify Ueberreiter's freezing-points with T_E values for a fixed (but unknown) τ value. In what follows, T_E and T_F are used interchangeably.

So far, the idea of polymer freezing-points has been developed in terms of thermodynamic concepts or of changes in times of relaxation (or orientation). It

TABLE II

Substance	T_F (Ueberreiter)	Approximate range over which high elasticity develops (T_E)
Unvulcanized rubber	−66° C	−50- −70° C
Polystyrene	+81° C	+70- +90° C
Polyisobutene	−65° C	−50- −70° C

is suggested here that this change, and also the development of high elasticity, correspond to a fundamental alteration in molecular dynamics, namely, the change from a considerably restricted to a relatively free rotation of the C−C bonds in the main polymer chain. The Mark-Kuhn kinetic theory of rubber is based on the idealized case of complete rotational freedom of these bonds, although this assumption has recently been questioned by Bresler and Frenkel[8]. It seems that comparatively free rotation is probably necessary to explain high elasticity, but that it needs extension in that it is developed only above different temperatures for individual polymers, this being the basic reason for the differences in their elastic behavior. A similar idea is implicit in Mark's recent work[9], but it is developed here in more detail.

This hypothesis is strongly supported also by the extensive work of Fuoss[10] on the dielectric properties of polar polymers. This author has noted that there is a sharp change in the electrical dispersion properties as the temperature is raised through the so-called brittle-point. The dielectric constant goes through an inflexion increase, and the a.c. loss factor reaches a maximum. The brittle-point concept is derived from the observed mechanical properties[11]; below it, the polymer breaks suddenly under an increasing load with no preliminary stretching, while above it, elastic extension and plastic flow occur before fracture. In terms of the ideas outlined in this paper, it is obvious that the change at brittle-point is the same as the onset of highly elastic deformation and, therefore, corresponds to T_E for a fairly small relative strain. (Hence, it will be generally lower than the value computed from other data.) Fuoss discusses the brittle-point in terms of an internal melting, but an explanation in terms of free

rotation seems more precise; a change of this sort would give the experimentally observed electrical results, and would also agree with his observation that, besides the expected change in the density-temperature coefficient on either side of the brittle-point, a discontinuity in the specific heats also exists[12].

MOLECULAR STRUCTURE AND ELASTIC BEHAVIOR

The next stage is to see whether there is any general qualitative connection between molecular structure and elastic properties. In a vinyl polymer of the type $(-CH_2-CXY-)_n$ or in one based on butadiene, the ease of rotation depends on the nature of X and Y and their interaction with adjacent similar groups, both on the same chain and on neighboring ones. In this treatment, only the free rotation of a single chain is considered, and it will be affected by two main factors—one of these is purely steric, due to the bulk size of the substituent groups, the other is electrical and is caused by the existence of dipoles on them. In general, the latter effect will be much larger, a fairly large bulk size of X or Y being necessary before free rotation is appreciably affected.

A considerable amount of insight can be obtained into the problem by a study of Fischer-Hirschfelder models of the polymers concerned. Polymers based on butadiene will first be considered, then vinyl types. For a natural rubber composed of isoprene units, free rotation is possible about all the C−C single bonds, the same being true for a butadiene chain (Buna rubber). In polychloroprene, free rotation is still possible as the adjacent halogen atoms, although strongly polar, are too far apart to affect each other, and this substance will have approximately the same elastic range as natural rubber, in agreement with experience[3]. The same is also true for hydrogenated and chlorinated rubber; in both cases, even more free rotation is possible as a result of saturation of the C=C bond, but for chlorinated rubber, the chlorine atoms are still too far apart to affect each other.

The various copolymers of butadiene and styrene (Buna-S) or acrylonitrile (Perbunan) will still have rotational freedom over a large proportion of C−C links as blocking will occur only if two hindering groups are adjacent. If x is the proportion of blocking constituent in the copolymer, the fraction of C−C bonds which are hindered can easily be calculated from the work of Wall[13]; it works out as x^2 of the whole (see Appendix). For the 2:1 styrene:butadiene copolymer ($x=0.66$) studied by Ueberreiter, the fraction comes to 0.43, so a large proportion of the C−C bonds is still free, in spite of the high percentage of styrene. This is borne out by the T_F values of Ueberreiter[14] (styrene= +81° C, styrene:butadiene 2:1 polymer= −70° C).

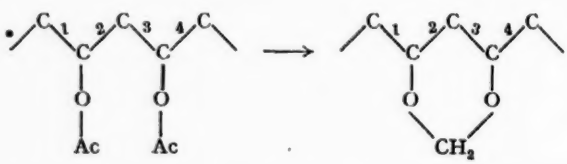
In pure vinyl polymers, the X and Y substituents are much closer together in adjacent groups, and hindrance effects become much more pronounced. A model of a polyisobutene chain $(-CH_2-CMe_2-)_n$ gives very little clearance for the side-chain methyl groups but, owing to their essentially nonpolar character, it seems likely that their interaction will be small and rotation not impeded. This would explain why high-molecular polybutenes have essentially the same elasticity range as natural rubber. If, however, the size of the substituent group is increased much, a purely steric effect enters, as with polystyrene (Y=H, $X=C_6H_5$). Hence, in this case, free rotation is not possible until a much higher temperature is reached ($T_F=+81°$ C, as opposed to −66° C for polyisobutenes).

If we now consider the effect of a single polar group (Y=H, X=polar), the general result will be to raise T_F, the extent, depending on the dipole interaction. For polymers, such as vinyl acetate and methyl acrylate, rotation is still com-

paratively free; the former polymer is elastic above ~40° C, and the latter still has rubberlike properties at room temperature. For both these molecules, the corresponding models show comparatively free rotation, but for a polyvinyl chloride molecule, the hindrance to rotation is very much more severe, owing to the strong C—Cl dipoles. This also corresponds to its behavior in practice, as it does not acquire elastic properties until ~100-110° C, without a plasticizer.

These ideas can now be extended to cover polymers of the type $(CH_2-CXY)_n$; if Y=H and rotation is partially restricted by the polar nature of X, hindrance can be very sharply increased by replacing the hydrogen atom at Y by a very slightly larger group, such as methyl. This is seen most strikingly if models of methyl acrylate and methacrylate are compared: the former is fairly free, whereas in the latter, rotation is badly hindered. The elastic properties of these two polymers are, moreover, in agreement with this observation, there being a very great contrast between their T_E values (methyl acrylate T_E < room temperature; methyl methacrylate T_E ~90° C). A similar contrast is found with polymers from methylvinylketone and methylisopropenylketone.

Rotation of the long-chain molecule will also be cut down if parts of it are linked up internally; this occurs in the process of acetalation, *i.e.*, in the formation of polyvinyl formals, acetals and butals from acetates.



Rotation about bonds 2 and 3 has been completely suppressed by this reaction, so for a highly substituted polyvinyl formal, the elastic transition only occurs at ~+115° C. (Part of this effect is, however, due to cross-linking[15], which is considered later.) For a less highly substituted acetal, a number of free links still remain and, hence, the elastic transition will be nearer to that of the pure acetate, as considerations similar to those discussed for the butadiene-styrene polymer apply here also.

THE EFFECT OF PLASTICIZERS

In the ideas outlined above, the effect of molecular structure has been considered chiefly in terms of the rotation of a single chain; this has been done deliberately to simplify the discussion, but it should be understood that the same general ideas apply when the interaction of different chains is studied.

If, as has been suggested, molecular interaction alone determines the development of high elasticity, the temperature range over which it occurs should be independent of the polymer chain-length: this has been shown by Ueberreiter[6], who finds T_F to be independent of chain-length for a series of widely varying high molecular polystyrenes and isobutenes. The same applies to ΔG and T_E, as defined previously; these quantities, however, will be affected by anything that cuts down interaction on a molecular scale, and this can be achieved by the introduction of a plasticizer or solvent. A fall in ΔG is observed, and T_E (or T_F) also falls proportionally. Evidence for this comes from several sources. Ueberreiter[6] finds that T_F for polystyrene is reduced as an increasing percentage of paraffin up to 10 per cent is added; thereafter, no further reduction occurs: this

seems probably due to a separation of two phases, as he himself suggests. Similar conclusions can be drawn from Fuoss' results[10] with the system polyvinyl chloride-biphenyl. Table III shows the effect of percentage plasticizer on T_E (for $\tau=1$ sec.) for methyl methacrylate polymers, taken from Alexandrov and Lazurkin's accurate data. Miller, Busse and Davies[16] have also measured the hardness of a number of plasticized polyvinyl chlorides at different temperatures by an indentation method. This type of measurement is rather crude, and gives only a comparative Young's modulus figure: however, the curves show the typical transition from ordinary to high elasticity, and from them, the temperature at which the modulus alters very rapidly can be estimated for different proportions of plasticizer. These correspond roughly to a fixed τ value, and are tabulated below. The decrease in T_E (and ΔG) for these two cases is roughly proportional to the percentage of plasticizer present (Table IV), and this may well be a general phenomenon in ideal one-phase polymer-plasticizer systems.

TABLE III

EFFECT OF PLASTICIZER ON METHYL METHACRYLATE POLYMERS

Percentage of plasticizer	T_E
0	125° C
10	87
30	50

TABLE IV

EFFECT OF TRICRESYL PHOSPHATE ON PVCl POLYMERS

Percentage of tricresyl phosphate	T_E
0	89
10	70
20	54
30	32
40	+ 7
50	− 10° C

THE EFFECT OF CROSS-LINKING

As seen above, any factor which decreases chain interaction or free rotation lowers ΔG and T_E (or T_F). The converse is true also. To explain the return of stretched rubber specimens to their original shape, it appears necessary to assume the existence of a small number of weak cross-bonds between the chains[17]. These may be caused by pure chain entanglements, but might be the result also of random local adlineations of neighboring chains. Whatever the cause, any increase in interchain connection hinders the average free rotation of the whole macromolecule and thus raises T_E or T_F. In rubber, this is done by vulcanization and, from Ueberreiter's results[6], the effect of various percentages of sulphur on a rubber is to increase T_F for a fixed period of vulcanization (Table V). It increases also with the time of vulcanization for a fixed percentage of sulfur. Similar results are also given for various styrene-divinylbenzene polymers (Table VI).

TABLE V

EFFECT OF VULCANIZATION ON T_F

Percentage of sulfur	T_F
0	− 65° C
0.25	− 64
10	− 40
20	− 24

TABLE VI

T_F FOR STYRENE-DIVINYLBENZENES

Percentage of divinylbenzene	T_F
0	+ 82° C
0.9	83
8.5	86
28	94
56	99
100	107

MOLECULAR STRUCTURE AND $D_{HE}(\infty)$

The effect of the variables discussed above on the absolute value of $D_{HE}(\infty)$ can be dealt with only briefly since, apart from the work of Alexandrov and Lazurkin, there exists little accurate data on the subject. The Mark-Kuhn theory gives for the Young's modulus for high elasticity the value $7RT\rho/M$, where M is the polymer molecular weight and ρ is its bulk density. It has been stated that this value gives reasonable values for M. The basic assumptions of this theory have been discussed by Frenkel[8], who gives an alternative formula which still contains the relationship $E_{HE} \propto 1/M$, but also introduces an interaction energy V_0 hinders free rotation. He derives $E_{HE} \propto 1/V_0$, and this approach would appear to be worth further consideration, since it represents a means of introducing the effect of molecular structure into E_{HE}. All that can be said at the moment is that, on both theories, $D_{HE}(\infty)$ increases with increase in the molecular weight. This is in agreement with the general qualitative observation that flexibility and allied properties are improved by an increase in molecular weight, but it is hoped to get more definite experimental data on this point in the future.

SUMMARY

The simple Mark-Kuhn theory of high elasticity of rubber has been extended, on the basis of the work of Alexandrov and Lazurkin, to cover the elastic properties of other polymers. The chief principle invoked is that high elasticity is developed only when rotation of the main C–C chain in the polymer is comparatively free. The effect of molecular structure, plasticizer and cross-links on elastic properties has been indicated, and also a connection with other observed physical properties, such as volume expansion, dielectric dispersion and specific heat.

APPENDIX

Let there be N_X and N_Y molecules of type X and Y in the chain. Let $x = \dfrac{N_X}{N_X+N_Y}$, the fraction of X in the chain.

If P_i be the number of groups containing i successive X's in the chain, then from Wall, we have

$$P_i = N_X(1-x)^2 x^{i-1}$$
$$= (1-x)^2 x^i \text{ total no. bonds in chain.}$$

If when two X groups are adjacent in the chain, the bond joining them is "frozen," then each group of iX is associated with $(i-1)$ "frozen" bonds.

$\therefore$ The number of frozen bonds is given by $\Sigma P_i(i-1)$ summed over all i from 1 to α. Substituting for P_i, we get for the fraction of "frozen" bonds,

$$\sum_1^\infty (i-1)(1-x)^2 x^i$$
$$= (1-x)^2 \left[\sum_1^\infty (i+1)x^i - 2\sum_1^\infty x_i \right]$$
$$= (1-x)^2 \left[\frac{1}{(1-x)^2} - 1 - \frac{2x}{1-x} \right]$$
$$= x^2.$$

This work has been carried out in the Department of Colloid Science, Cambridge, and the author wishes to record here his best thanks to Professor E. K. Rideal for many stimulating discussions during the period in which the ideas expressed above have been developed.

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THE KINETICS OF RUBBERLIKE ELASTICITY *

D. D. ELEY

DEPARTMENT OF COLLOID SCIENCE, THE UNIVERSITY, CAMBRIDGE, ENGLAND

During recent years a molecular treatment has been developed by a number of authors, notably Meyer, Mark, and Kuhn[1], to account for the exceptional stress-strain-temperature relationships shown by rubber and similar high polymers, under equilibrium conditions. Briefly, in its unstrained state the long chains assumed a curled-up configuration, according to theoretical calculations of probability. If now a stress is applied, the long chains uncurl and adlineate along the axis of extension, this orientated state being one of lower probability. If ΔS is the entropy difference between the two configurations for a given percentage extension, then $T\Delta S$ may be equated to the free energy of extension, and a Young's modulus calculated in good agreement with experiment. A main assumption in this treatment is that in an isolated polyisoprene chain free rotation about C—C bonds is permissible, and this has recently been questioned by Frankel[2]. This author has given a formula for Young's modulus of high elasticity, E_{HEL_∞}, involving the energy of rotation about a C—C bond in an isolated chain, which lies in the range 3 to 3.6 k.cal. per mole.

RATES OF DEFORMATION

In this paper we are, therefore, not concerned with equilibrium conditions in elastic phenomena, but with the rates at which these equilibria may be reached; that is, we are concerned with relaxation times in rubber. We shall consider only moderate extensions, *i.e.*, up to 400 per cent, and therefore exclude a consideration of crystallization and other complicating phenomena which are apparent at higher extensions[3]. If a piece of rubber be stressed it is legitimate to separate the deformations into a number of components and, to date, this has been done in two ways. Kuhn[4] considers the material as subjected to unit strain, and then the instantaneous value of the stress, f^o (*i.e.*, the stress measured an infinitely short time after the application of the strain) is taken as the sum of the stresses arising from the separate bonding mechanisms, f_{10}, f_{20}, etc., *i.e.*:

$$f_0 = f_{10} + f_{20} + f_{30} \tag{1}$$

Each of these component stresses is supposed to decay with time to zero, according to Maxwell's relation, the rate of decay in each case being characterized by a relaxation time λ_1, λ_2, etc., and the stress at time t being given by:

$$f_t = f_{10}\, e^{-t/\lambda_1} + f_{20}\, e^{-t/\lambda_2} + \tag{2}$$

Alternatively, the observed Young's modulus at time t is:

$$E(t, T) = E_{10}\, e^{-t/\lambda_1} + E_{20}\, e^{-t/\lambda_2} + \tag{3}$$

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We write $E(t, T)$, since the relaxation times are strongly dependent on temperature, to a first approximation following $\lambda = Ae^{-E/(RT)}$. For polymers like rubber Kuhn writes:

$$E(t, T) = \sum_{1}^{n} E_{no}\, e^{-t/\bar{\lambda}} + E_{ko}\, e^{-t/\lambda_k} \tag{4}$$

where E_1, E_2 . . . E_n represents a number of Young's moduli, all with high values in the range 10^2-10^4 kg. per sq. mm., corresponding to the separation of the chains against the Van der Wall's forces. To these mechanisms he gives an average relaxation time $\bar{\lambda}$. E_{ko} is the Young's modulus of high elasticity (already referred to as $E_{HEL\infty}$), which arises from the orientation of the chains, and has a value of about 0.2 kg. per sq. mm. These E values are only slightly dependent on temperature, compared to the λ's. Briefly then, for $t \ll \lambda$, E has the high value given by $\sum_{1}^{n} E_{no}$. For a given value of t (say 1 second), as T is raised, $\bar{\lambda}$ becomes smaller, until at about $-50°$ C, the first term in the expression has become vanishingly small, and $E(t, T)$ is given by $E_{ko}\, e^{-t/\lambda_k}$, where $e^{-t/\lambda_k} \sim 1$. Further rise in temperature produces little effect until λ_k becomes small, when $E(t, T)$ drops to zero, and viscous flow is observed. So briefly we may say that orientation of the chains is hindered by their lateral forces of cohesion, for a value of t of 1 second, only at $-50°$ C do the chains possess sufficient thermal energy to overcome these forces and assume the oriented form (later we shall show that $\bar{\lambda}$ also involves rotation around C—C bonds). In the region of room temperature, the oriented chains in the stretched state are held together by a number of chemical bonds (in lightly vulcanized rubber, about 1 cross-bond per 100 chain links), which successfully resist permanent deformation; that is λ_k is large. At higher temperatures these chemical bonds start to break, so the chains may slide irreversibly over each other.

Kuhn's treatment may be compared advantageously with that given more recently by Alexandrov and Lazurkin[5]. These latter authors consider a specimen subject to unit stress, and then sum the component deformations. It is not our purpose to discuss at present the fundamental differences between these two methods. Kuhn's treatment corresponds to a number of spring plus dash-pot elements (each spring and dash pot in series) in parallel, whereas the Russian authors' treatment corresponds to spring plus dash pot in series. In point of fact it is doubtful if the molecular forces may be summed in either of these two extreme ways. However, the treatment of Alexandrov and Lazurkin appears a more useful theory for consideration of extension or compression data. They consider the elastic deformation for unit stress as made up of a component of ordinary elasticity, arising from a separation of the chains, which they call D_{OEL}. and one arising from the orientation of the chains giving rise to high elasticity, D_{HEL}. Then:

$$D(t, T) = D_{OEL} + D_{HEL} \tag{5}$$

The development of D_{HEL} involves orientation of the chains, *i.e.*, it involves their passage over a potential barrier arising from the interatomic forces, and this they treat as a unimolecular reaction. If $D_{HEL\infty}$ be the equilibrium deformation at infinite time, then:

$$D_{HEL} = D_{HEL\infty}\,(1 - e^{-t/\tau}) \tag{6}$$

We refer to τ as the orientation time; it is the time required for the strain at constant stress to reach a fraction $\left(1 - \frac{1}{e}\right)$ of a definite equilibrium value. It is to be distinguished from the relaxation time of Maxwell as used by Kuhn, which characterizes the rate of dissipation of stress to zero at constant strain. However, a comparison of the two treatments shows immediately that τ is analogous to $\bar{\lambda}$, the mean value of the relaxation times associated with the bonding mechanisms of high Young's moduli, in Kuhn's treatment. The authors further write $\tau = Ae^{\Delta H^*_{el}/(RT)}$, and show that these simple relations give an adequate account of the deformation, temperature, time relations for rubber and a number of other polymers, at moderate strains. By adding a term for viscous flow to the equation of Alexandrov and Lazurkin, it is possible to write the full equation for deformation D, at a constant stress f:

$$D(t, T, f) = \frac{f}{E_{OEL}} + \frac{f}{E_{HEL_\infty}}(1 - e^{-t/\tau}) + \frac{tf}{\eta} \qquad (7)$$

Here E denotes Young's modulus, and η the apparent viscosity, which may be a function of f (now-Newtonian flow). This equation is restricted to conditions where crystallization phenomena can be neglected.

THE SLOW PROCESS IN ELASTICITY AND VISCOUS FLOW

There are few reliable data on elasticity and plastic flow in the same polymer specimen, since elasticity is most easily investigated under conditions where no flow occurs, *e.g.*, as in lightly vulcanized rubbers. It is not, however, our purpose to attempt to compare the two mechanisms under the same conditions. Rather we shall compare the data on elastic-rates in lightly vulcanized rubber with data on the viscous flow in unvulcanized rubber. Since the latter has received a fairly comprehensive treatment recently, from the point of view of the transition-state theory of chemical reaction[6], it should be possible to derive information about the rate-step in elastic deformation.

Alexandrov and Lazurkin present data for a number of polymers, as plots of $\log \tau$ against $1/T$, from which ΔH^*_{el} in $\tau = Ae^{\Delta H^*_{el}/(RT)}$ can be simply calculated. In what follows we use the full equation[6]:

$$k = \frac{\kappa T}{h} e^{-\Delta G^*/(RT)} = \frac{\kappa T}{h} e^{+\Delta S^*/(RT)} e^{-\Delta H^*/(RT)} \qquad (8)$$

Applying this equation to the elastic rate process ($k = 1/\tau$), then ΔG^*_{el}, ΔH^*_{el}, ΔS^*_{el} are the Gibbs' free energy, heat content change, and entropy of activation, respectively, for this process. The experimental data appear to bear out the assumptions of a unimolecular orientation process, with a value of ΔH^*_{el} independent of the elongation[7]. Further, for our purposes, ΔS^*_{el} and ΔH^*_{el} may be assumed independent of temperature. The table gives a list of these values.

Now ΔH^*_{el} may be divided into two separate contributions, ΔH_{el} (1) and ΔH_{el} (2).

ΔH_{el} (1).—The center of gravity of the orienting unit of the chain has to move in the orientation process. For this purpose, the neighboring chains must be separated from the chain under consideration, against the forces of cohesion (Van der Waal's forces). This involves an internal energy change, which depends on forming a hole in the polymer of sufficient size to enable the unit as a whole to move as a free chain. The term may be looked upon as a steric energy arising

from external factors, and when so freed, the chain unit can move from one equilibrium position to another one. The latter position corresponds to an increased degree of orientation in the direction of stress.

ΔH_{el} (2).—For the free chain-unit to be fully oriented, it is necessary for rotation to occur about C—C bonds, so the segment may uncurl and assume its fully stretched out condition. If we take a rough value of the energy of activation for rotation as 3 k.cal. per C—C bond[2], then this term is $3n$ where n bonds have to be rotated.

So in the activated state for orientation we visualize the chain-unit as freed from its neighbors, and possessing free rotation about all or a fraction of its C—C bonds.

To evaluate term ΔH_{el} (1), we refer to Eyring and Kauzmann's theory[8] of the viscous flow of linear polymers. Eyring treats viscous flow as the passage of the flow unit (for simple liquids, a molecule) from one equilibrium position in the liquid to the next position. For simple liquids, the activation energy for this process is about one-quarter the latent heat of evaporation, and may be equated to the energy required to form a hole of sufficient size for the jump to occur. With increase in chain-length, however, the value of $\Delta H^*_{visc.}$ (in the equation for viscosity derived from the fundamental rate Equation (8)) does not con-

TABLE I

Polymer	ΔH^*_{el} k. cal. mole^{-1}	ΔS^*_{el} ca. deg.$^{-1}$ mole^{-1}	ΔG^*_{el} k. cal. mole^{-1}
Natural rubber + 3% sulfur	38	104	7
Chloroprene	38	99	8.5
Partly vulcanized ebonite	55	121	19
Polymethacrylate + 30% plasticizer	52	87	26
Polymethacrylate + 10% plasticizer	59	95	31
Polymethacrylate without plasticizer	75	122	39

tinually increase, but reaches a maximum of about 10 kilocalories per mole. Flory[9] has shown that, for a number of condensation polymers, $\Delta H^*_{visc.}$ is about 8 kilocalories mole^{-1}, independent of their weight average molecular weight. This corresponds to a heat of evaporation per flow unit of 32 kilocalories mole^{-1}, and comparison with the evaporation heat of the monomer suggests to Eyring that viscous flow occurs in this case through the movement of segments of about 30 chain atoms. Similarly, Smallwood[10] and Eyring[8] have shown, from Mooney's[11] data on viscous flow in raw rubber, that $\Delta H^*_{visc.} = 10.2$ kilocalories, corresponding to a segment size of 40 chain carbon atoms. This upper limit of 10 k.cal. for $\Delta H^*_{visc.}$ for linear polymers appears well established; it does not, however, hold for globular molecules, *e.g.*, asphalts, with $\Delta H^*_{visc.} \sim 40$ kilocalories[12], or chains with numerous cross-bonds, *e.g.*, linear P—F polymers, which have hydrogen bonds, and possess $\Delta H^*_{visc.} \sim 80$ kilocalories[13]. Vulcanization of rubber, may, of course, lead to enhance values of $\Delta H^*_{visc.}$. We note also that the data of Ferry and Parks[14] on polyisobutene, which lead to the high values of $\Delta H^*_{visc.}$ of 14 to 23 kilocalories per mole, are probably complicated by elastic phenomena. A confirmation of the above value for rubber can be obtained from Treloar's[15] experiments, in which the amount of plastic flow is measured over one hour at constant extension, for 25° and 50° C. For the crepe rubber used, we roughly calculate $\Delta H^*_{visc.} = 10.9$ kilocalories (160 per cent extension) and 7.0 kilocalories (250 per cent extension).

So we may say that, in viscous flow, a rubber chain moves by segments of about 40 chain atoms, that is, 10 isoprene units, as determined from experiments

where a minimum of cross-bonds are present. This segment size is based on $\Delta H^*_{visc.} = 10$ kilocalories, and the assumption either of no rotation about C—C bonds or that rotation about C—C bonds involves no energy of activation. The last assumption is hard to defend, and Frenkel has pointed out the possible importance of rotational isomers in effecting the equilibrium Young's modulus. At the present time it seems reasonable to attribute an activation energy of about 3 kilocalories for rotation of a C—C bond. Where polar or bulky side groups are present, this value must be augmented. The first assumption is more reasonable. The segment as a whole may be considered to move in viscous flow without rotation of C—C bonds, except that one bond which joins it to the rest of the molecule. This means that, in viscous flow, the segments of the molecule move forward in a random fashion, without the segments themselves suffering any change of shape.

At the present time, no fundamental reason is given by Eyring as to why the empirical segment size of a chain molecule has its particular value. There seems no reason, however, to postulate two different segment sizes for a given polymer showing two different types of internal friction. Reverting to the value of ΔH^*_{el} of 38 kilocalories for lightly vulcanized rubber, there seems no reason why the segment size here should differ from that obtaining in the viscous flow of raw rubber. The chain constitution is the same, and in both cases we are concerned with the motion of a chain segment through the restraining field of identical Van der Waal's forces. Therefore we must attribute about 7 kilocalories (10 − 3, allowing for the rotation of one bond) to the first contribution to ΔH^*_{el}, ΔH^*_{el} (1). It is then clear immediately that the extra 31 kilocalories must arise from rotation around the C—C bonds. This would correspond to rotation about 10 C—C bonds, *i.e.*, one C—C bond must be rotated per isoprene unit in the segment for the chain to assume its fully stretched-out condition.

EFFECTS OF CROSS-BONDS

The primary effect of small degrees of vulcanization on rubber is to suppress plastic flow, but not to effect the elasticity appreciably. The table previously given shows, however, that if appreciable numbers of cross-bonds are introduced, as in partly vulcanized ebonite, ΔG^*_{el} increases. Clearly this is to be associated with the increase in ΔH_{el} (1), the energy required to free the segment from its neighbors, and it is difficult to see that the internal rotation of the segment ΔH_{el} (2) will be appreciably affected by the presence of relatively small numbers of chemical cross-bonds. Primarily this increase in ΔG^*_{el} will be noticeable in an increased temperature, to which the rubber has to be raised before it will show unit deformation when subjected to unit stress for unit time. In considering polymethacrylate (see the table) we note that the lateral forces of cohesion between the chains are greater here than in rubber, as a result of the polar side groups. So elasticity develops only at higher temperatures for this polymer, ΔG^*_{el} being high. This high value of ΔG^*_{el} is due partly to a high value of ΔH_{el} (1) and partly to an increased potential barrier for internal rotation, if equal segment sizes be assumed for the two polymers. The data on the effect of plasticizer enables us to separate out the two effects roughly. The plasticizer molecules clearly act in such a way as to space out the chains, and lower ΔH^*_{el} (1), while it is difficult to see that they can have an equally important effect in reducing steric hindrance to internal rotation. The data given suggest that, at about 40 per cent plasticizer, the chain segments for the most part no longer touch each other; this corresponds to an extrapolated value of ΔH^*_{el} of 50 kilocalories.

Therefore we may attribute the extra 25 kilocalories present in unplasticized polymethacrylate as arising from ΔH_{el} (1). The difference between 50 kilocalories and the rubber value of 38 kilocalories may then be attributed to the energy of internal rotation, *i.e.*, if, as in rubber, 10 bonds per segment are assumed to rotate in methyl methacrylate, there is an extra 1.2 kilocalories per bond required over the simple isoprene chain.

This separation is to some extent artificial for dipole bonds, since the internal rotation of such a chain, freed from the steric repulsion forces of its neighbors, still experiences a restriction arising from the dipoles in the neighboring chains. A part of the extra 1.2 kilocalories per bond may well arise from this factor. In a full treatment the frictional effect of the plasticizer molecule would also need to be considered.

The values of ΔG^*_{el} are clearly determined by ΔH^*_{el}, since, although ΔS^*_{el} tends to compensate ΔH^*_{el} in the usual fashion, the variations in it are too small to dominate the ΔG^*_{el} term. This means that, in the activated state, the increased degree of freedom of the orientated chain and its neighbors is always roughly the same, corresponding to $\Delta S^*_{el} \sim 100$ cal. deg.$^{-1}$ per mole (of orienting unit). Now Eyring[8] has shown, from Flory's data already cited, that for viscous flow of linear chains, at any rate for the condensation polymers considered that $\Delta S^*_{visc.} \sim -0.5Z^{\frac{1}{2}}$, where Z is the weight average molecular weight. This he plausibly explains as a term dependent solely on the coöperation of the movements of all segments of the molecule necessary for viscous flow. The actual segment itself in its activated state has an entropy which is little greater than in its initial equilibrium position. Of the two explanations for this, namely (1) completely free rotation in the initial state and transition state, and (2) a similar relatively small amount of rotation in both states, the latter seems more likely. For the raw milled rubber mentioned, the experimental $\Delta S^*_{visc.} = -42$ cal. deg.$^{-1}$ mole^{-1} leads to a chain length of 7000 carbon atoms. In the case of elastic orientation a similar negative entropy term, arising from a coöperation of the segments, must be considered, but this will correspond only to about 100 carbon atoms, *i.e.*, the number between two cross-links of sulfur. This contribution may then be estimated as -6 cal. deg.$^{-1}$ mole^{-1}, and so the full value of $\Delta S^*_{el} \sim 100$ cal. deg.$^{-1}$ mole^{-1} must mainly be associated with the onset of 10 free rotations in the segment. This value is high, but not unreasonably so.

CONCLUDING REMARKS

The data on dielectric dispersion give to some extent qualitative support to the considerations outlined above. For a maximum effect it is clearly necessary that all the dipoles in a linear polymer should follow the field as rapidly as possible, subject to the restrictions imposed by their being attached to a main valency chain. We may expect this chain to show segmental movement, and it is clearly necessary that here, as in the case of orientation elasticity, a certain degree of freedom of internal rotation of the segment is necessary. Rubber is nonpolar and shows no dielectric dispersion but, in a series of papers, Fuoss[16] presents a full analysis of polyvinyl chloride systems. It appears that the rate process for dispersion in unplasticized polyvinyl chloride has an activation energy of 43 kilocalories, which is sufficiently high to suggest the presence of contributions due to internal rotations. On the other hand, below the brittle point it is only 2.45 kilocalories, and, as Fuoss points out, segmental movement (high elasticity, viscous flow) is inappreciable at these temperatures. The slow process

at these low temperatures is most probably simply the rotation of the —CHCl— group in the chain, under the influence of the applied field.

This paper has been restricted to a discussion of elastic properties in the range where crystallization is unimportant. Now crystallization is known to affect both the equilibrium stress-strain relation and also the rates at which it is reached (due to a slow velocity of crystallization[3]). The latter problem appears too difficult to attempt at the present time, but a suggestion may be made with respect to the former. The percentage crystallinity in rubber is a function of temperature and deformation $C(T.\ d)$. Theoretically this function cannot be determined at present, but empirically it might be obtained from double refraction[17], or X-ray data. Now crystalline rubber may be expected to show comparatively small elastic effects (only separation of chains and bending of valency angles), and its irreversible flow under stress is to be looked upon more as a gliding than a viscous process, and to be relatively small. Then, at any rate for small percentages of crystallinity, we might consider a system of small crystals dispersed in the random long chains, in which the deformation of the crystals may be completely neglected, *i.e.*, they act purely as a diluent. Then we might adapt Equation[8] for deformation at constant stress in the following way:

$$D(t,T) = \frac{f}{E_{\text{OEL}}} + (1 - C)\frac{f}{E_{\text{HEL}_\infty}}(1 - e^{-t/\tau}) + (1 - C)\frac{tf}{\eta}.$$

Here C is the empirically determined function. This possibility will be examined in the future.

SUMMARY

1. The treatments of relaxation phenomena in polymer systems, due to Kuhn, and Alexandrov and Lazurkin, are outlined and discussed.

2. Eyring's rate equation is used to analyze the rates of orientation of long-chain molecules in a stressed specimen of lightly vulcanized rubber. The data are compared with similar data on viscous flow in raw rubber, and it is suggested that the segment size for movement is the same in both cases. In viscous flow, the segmental movement occurs without appreciable internal rotation within the segment. In elastic orientation, however, it appears that a high degree of internal rotation within the segment accompanies the formation of the activated state.

3. The activation energy for the orientation of long chains is separated into two terms: (1) the energy required to free a segment from its neighbors, (2) the energy of activation for rotation around C—C bonds. It is suggested that the main effect of vulcanization and plasticizers is on term (3); vulcanization tends to increase this term, plasticizers to decrease it.

4. Data on the dielectric dispersion of polyvinyl chloride suggests the need for internal rotational activation in this case, as in orientation elasticity. This is in agreement with what we should qualitatively expect. Possible complications due to crystallinity in rubber at high extensions or low temperatures are briefly discussed.

My best thanks are due to Professor E. K. Rideal, for his helpful advice during the course of this work. I am also indebted to R. F. Tuckett for many interesting discussions.

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IV. THE MICELLAR THEORY OF THE STRUCTURE OF RUBBER *

G. GEE

THE BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION, WELWYN GARDEN CITY, HERTFORDSHIRE, ENGLAND

The molecular weight data reported in Part II[1] depend on the assumption that the values obtained by extrapolating osmotic pressure measurements to infinite dilution represent true molecular weights. This point of view has been strongly criticized, particularly by Pummerer and his coworkers[2], according to whom rubber normally exists in solution in the form of micelles comprising more or less well-defined aggregates containing a considerable number of chemical molecules. The osmotic "molecular weight" is then regarded as the weight of an average micelle. If they exist, these micelles may be important in determining both the chemical and physical behavior of rubber, for we should clearly expect the bonds by which the chemical molecules are bound into micelles to be weaker than those within the molecules. It may be noted that it has been shown elsewhere[3] that the physical properties of a series of rubber fractions are closely related to their osmotic and viscosity molecular weights. Since, according to the micellar theory, these fractions can differ only in micelle size, their mechanical behavior must, from this viewpoint, be determined by the size of the micelles, which must therefore remain intact during mechanical deformation of the rubber. It is the object of the present paper to examine in more detail the basis of the micellar theory, and especially to offer an interpretation of the results of the Rast method, on which Pummerer's arguments are mainly based.

The Rast method is a well-known microanalytical technique for the determination of molecular weights, and consists in measuring the depression of the freezing point of camphor produced by the substance examined. Applied to rubber, it has given somewhat variable results in the hands of different workers[2, 6], but there is general agreement in indicating a molecular weight of the order of 1 per cent of that obtained from osmotic data. A number of objections to the method have been raised[4], but they are concerned only with relatively minor corrections, and thus do not affect the main problem, which is that of the order of magnitude of the molecular weight. Similarly low values of molecular weight have been calculated from the freezing-point depression in menthol solutions[5], but it has been shown[6] that the freezing point of menthol itself varies with the rate of crystallization by an amount comparable to the rather small depressions produced by rubber. It seems preferable, therefore, to confine our attention to camphor, in which case, on account of the very large cryoscopic constant, the low molecular weight is more certainly proved.

There is a two-fold experimental basis for the view that camphor and related solvents differ from benzene in that they are capable of giving true molecular dispersions of rubber. (1) It has been stated[7] that rubber dissolves rapidly in camphor and menthol, without previous swelling, and gives mobile solutions. (2) Evidence has been presented[2] to show that, in distinction to the results of

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osmotic and viscosity methods, the molecular weights found by the Rast method are independent both of the type of rubber and the concentration of the solution.

Two aspects of the Rast method call for comment: (1) the actual method of carrying out the experiments, and (2) the interpretation of the results obtained. The most obvious objection to the Rast procedure is that it involves heating together camphor and rubber at a temperature of about 180° C. Our first experiments showed that, in the presence of air, rapid and extensive degradation occurred. After heating with camphor in a sealed tube for 30 minutes at 180° C, the viscosity molecular weight of crepe (determined in benzene) had fallen to one-sixth and on longer heating (1 to 2 hours), a brown oily substance distilled onto the cooler parts of the tube. This degradation was completely prevented by evacuating the tube carefully before heating and, when this was done, the rubber dissolved only after heating with camphor for several hours, giving first a swollen gel and finally a typical rubber solution of high viscosity (a 7 per cent solution of sol rubber in camphor at 180° C was too viscous to flow). This simple observation alone disposes of the first part of the evidence in favor of a micellar structure for rubber. It also makes clear that, if the freezing points of rubber-camphor solutions are to be measured at all, a vacuum technique is essential.

In its simplest form, the Rast method consists in determining the melting point of camphor and of camphor plus rubber by the usual melting point tube method employed in the identification of organic substances. This procedure does not readily lend itself to vacuum operation, even if its accuracy were sufficient for the present purpose. Reilly and Rae[8] have described a more precise modification, based on the determination of cooling curves for the solvent and solution. The design of an apparatus in which this can be done *in vacuo* is conditioned by the necessity of heating the whole of the evacuated portion to prevent rapid sublimation of camphor; the design finally adopted is shown in Figure 1.

The thermometer (an Anschütz type graduated to 0.1°) was completely enclosed in the evacuated tube. It was suspended from a tungsten hook and centered in the solution compartment by a constriction in the body of the tube. The side tubes A were provided so that the solution could be concentrated by distilling off camphor without opening the tube; the amount removed was determined by sealing off the side tube into which the camphor had been distilled, and weighing its contents. Four side-tubes were employed in the final series of measurements, rendering possible observations at 5 concentrations with a single filling. Rubber was introduced through B in the form of a benzene solution, which was evaporated to dryness and finally evacuated thoroughly at 50-60° C before weighing in the camphor, reëvacuating, and sealing off B. The tube was completely immersed in liquid paraffin in a cylindrical Dewar vessel of internal diameter 5 cm. This bath was heated electrically by a wire wound as uniformly as possible on a glass tube fitted fairly closely into the Dewar and extending practically the full depth of the bath. A spacing of about 1 cm. between the turns of wire was sufficient to enable the important temperature range to be read accurately. The oil was efficiently stirred by a stream of nitrogen, and the heater current maintained constant by manual adjustment. In plotting a cooling curve, the heater current was adjusted so as to make the rate of cooling of the melt 0.2 to 0.4° per min.: higher cooling rates did not give sharp breaks in the cooling curve, while lower rates were difficult to maintain constant. The thermometer was read every ¼ minute through a lens, mounted in a tube to reduce parallax errors.

The camphor employed was a commercial specimen purified by resublimation

in vacuo at 100° C. Its freezing point was repeatable on successive determinations to better than 0.1°; removal of about half of the camphor by distillation did not change the melting point of the remainder significantly. With separate assemblies of the apparatus the melting point of the camphor could be reproduced to about 0.1° C. Difficulties were encountered when rubber solutions were employed; repeated attempts failed to give consistent results for solutions of crepe, sol rubber or an intermediate fraction[9]. The trouble undoubtedly arose from the high viscosity of the solutions, which made it impossible to be sure that the solutions were homogeneous, and also retarded the attainment of thermal

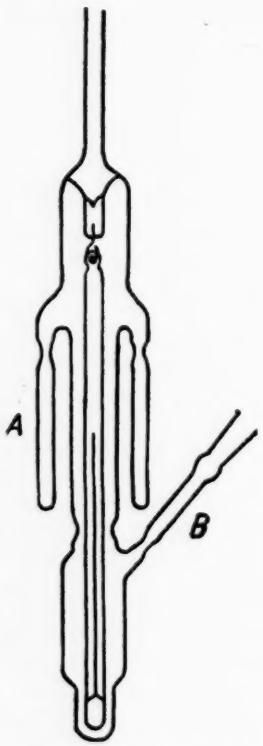

FIG. 1.—Freezing point tube.

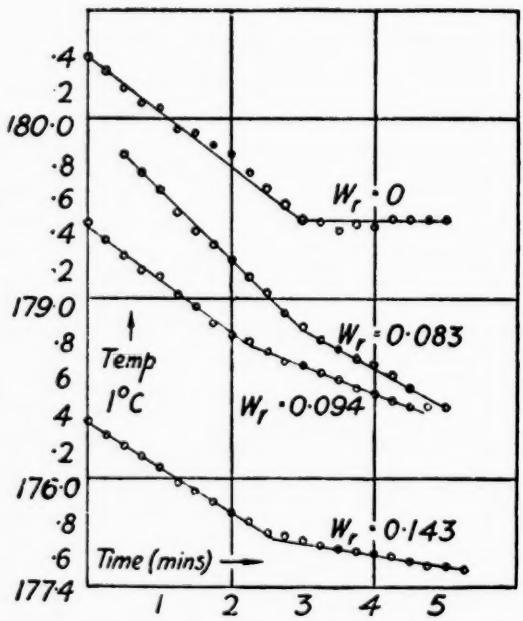

FIG. 2.—Cooling curves for camphor and rubber solutions.

equilibrium. More successful results were obtained with a heavily milled crepe, but the final experiments were carried out with a thermal degradation product prepared by Bolland[10], to whom my thanks are due. This material had a viscosity molecular weight of 53,000, and an osmotic molecular weight of 34,000, both measured in benzene plus 15 per cent methanol[1]. Camphor solutions containing up to 15 per cent rubber (by weight) were reasonably mobile, and their cooling curves showed sharp breaks: some typical results are given in Figure 2.

In this range of concentration the freezing points were reproducible to about 0.1°, giving a probable error of 0.2° in the depression. At higher concentrations the error increased rapidly and the cooling curve of a 19.8 per cent solution showed no detectable break: the figure given in Table I was estimated from the

temperature at which crystallization spread through the solution surrounding the thermometer, and may easily be in error by 1°. The freezing point depressions θ are given in Table I as a function of the weight fraction w_r[11] of rubber for 2 separate series of measurements.

The apparent molecular weights M' were calculated from the equation[12]

$$10^{-3} M' = \frac{40}{\theta} \cdot \frac{w_r}{1 - w_r} \tag{1}$$

They are several times larger than those previously reported[2], and are clearly not independent of the concentration, even allowing for the somewhat large experimental error at the lower concentrations. Similar results were obtained in the less accurate measurements made with milled crepe solutions.

TABLE I

Series 1			Series 2		
w_r	θ	$10^{-3} M'$	w_r	θ	$10^{-3} M'$
0.105	0.75	6.2	0.083	0.60	6.1
0.198	4.5	2.2	0.094	0.74	5.6
—	—	—	0.106	0.74	6.4
—	—	—	0.143	1.8	3.7
—	—	—	0.161	3.2	2.4

DISCUSSION OF RESULTS

The depression of the freezing point of a liquid arising from the presence of a solute is one of the "colligative properties" of the solution. Provided the solid phase in equilibrium with the solution consists of pure solvent[13], the depression θ may be shown by purely thermodynamic arguments to be related to the reduced vapor pressures of the solution[14]:

$$\theta = \frac{RT^{\circ 2}}{L_F^{\circ}} \ln p_o^{\circ}/p_o{}^{15} \tag{2}$$

where

T° = freezing point of solvent.
L_F° = molar latent heat of fusion of solvent.
p_o° = vapor pressure of solvent } measured at the same temperature (T°) and pressure.
p_o = vapor pressure of solution }

The osmotic pressure of the solution (Π) is also a thermodynamically related quantity[16]:

$$\Pi = \frac{RT}{V_o} \ln p_o^{\circ}/p_o \tag{3}$$

where V_o is the partial molar volume of the solvent in the solution.

The colligative properties cannot be related by purely thermodynamic argument with the molecular weights of the components of the solution. Their use to calculate molecular weights therefore involves the introduction of a physical hypothesis, which we normally do by assuming Raoult's law to apply. If N_o is the mole fraction of solvent in the solution we thus obtain:

$$\ln \frac{1}{N_o} = \ln p_o^{\circ}/p_o = \frac{L_o^F}{RT^{\circ 2}} \theta = \frac{\Pi V_o}{RT}. \tag{4}$$

Assuming $1 - N_0 \ll N_0$ and expanding:

$$\ln \frac{1}{N_0} \cong \frac{M_0}{M_r} \cdot \frac{w_r}{1 - w_r} \tag{5}$$

where w_r is the weight fraction of rubber in the solution and M_0 and M_r are the molecular weights of the solvent and the rubber. Any combination of Equation (4) with Equation (5) gives a thermodynamically identical method of obtaining the molecular weight of the solute.

It is well known that, in general, rubber solutions do not show ideal osmotic behavior, though the degree of departure from ideality may vary from solvent to

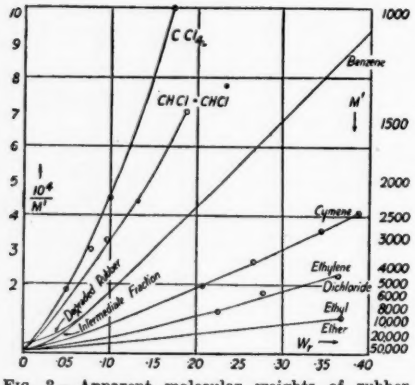

FIG. 3.—Apparent molecular weights of rubber in various solvents.

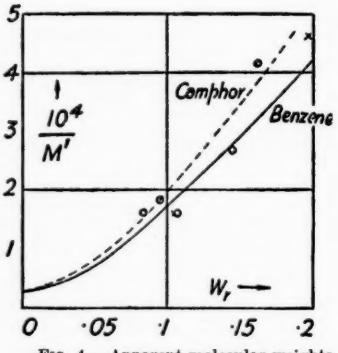

FIG. 4.—Apparent molecular weights of degraded rubber in camphor and benzene solutions.

solvent[1]. To overcome this difficulty, osmotic data are extrapolated to infinite dilution before applying Equation (4) in the limiting form:

$$M_r = \frac{M_0 RT}{V_0} \lim_{w_r \to 0} \left(\frac{w_r}{\Pi} \right). \tag{6}$$

In calculating molecular weights from Rast data, we do not extrapolate, but use the freezing point depression measured at a given concentration. This is precisely equivalent to calculating the molecular weight from the osmotic pressure or swelling pressure of a rubber solution or gel, or from the vapor pressure of a gel. Some values obtained in this way for a number of solvents are given in Figure 3, in which the reciprocal of the apparent molecular weight (M'), calculated from Equations (4) and (5), is plotted against w_r. The figures for benzene are obtained from osmotic and vapor pressure data on two samples of rubber[17], an intermediate fraction from latex[9] and the same degradation product that was employed in the camphor measurements. These figures are accurate over the whole range of w_r, but the remaining data of Figure 3 are calculated from Posnjak's measurements of swelling pressure[18], extrapolated to give the same molecular weight at infinite dilution, and are therefore only very approximate at low values of w_r. The relative positions of the curves cannot be seriously in error.

There are two conclusions to be drawn from this diagram:

(1) By a suitable choice of concentration any "molecular weight" may be found (within a very wide range) from experiments in one and the same solvent. The range available certainly covers the values found in camphor solutions (Table I).

(2) Comparing the data obtained in benzene for a highly degraded rubber and the "intermediate fraction", it is evident that the apparent molecular weight at a given concentration is practically independent of the nature of the rubber, unless the comparison is made in dilute solution.

The similarity of these results to those obtained with camphor solutions is brought out more clearly in Figure 4, which compares directly the apparent "molecular weights" of the degraded rubber in benzene and in camphor over a range of concentrations. It is evidently not possible to extrapolate the camphor data to infinite dilution, but they are at least consistent with the dotted line drawn, which would mean that camphor differed from benzene only in giving a slightly different degree of departure from ideal behavior.

Summarizing, we may state with confidence that camphor shows completely normal behavior as a rubber solvent, and that the "molecular weights" calculated from the Rast method are unrelated to the true size of the rubber molecule. The whole of the evidence in support of a micellar structure for rubber has been shown to be unsound, and we must conclude that the osmotic units whose size we have previously recorded are in fact true macromolecules.

The work described in this paper forms part of the program of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

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[11] Calculated from the weights of rubber and camphor introduced, corrected for the weight of camphor vapor in the tube.
[12] The cryoscopic constant is the same as that employed by Pummerer[2].
[13] If some solute also separates, the depression will evidently be smaller than that given by Equation (1).
[14] Guggenheim, "Modern Thermodynamics", Methuen, London, **1933**, p. 121, Equations (567) and (575).
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PHASE TRANSITION AND ELASTIC BEHAVIOR OF HIGH POLYMERS *

H. MARK

POLYTECHNIC INSTITUTE, BROOKLYN, N. Y.

Present experimental knowledge indicates that linear or moderately branched and cross-linked high polymers are capable of undergoing two types of phase transitions.

(1) A first-order transition, characterized by a sudden change of quantities such as specific volume, energy, and entropy, which may be briefly called a "crystallization" (or fusion). The crystallized areas formed in the course of this process are mostly elongated cylindrical or flat bundles of parallelized chainlike molecules, or segments of them, with an average length between 500 and 5000 A.U. and an average diameter of 50-200 A.U. They do not have plane and sharp boundaries, but they represent only regions of higher geometrical order and presumably go over gradually into the mesomorphous and amorphous parts, which approach the structure of a liquid. It seems that one and the same chain can extend through such a crystallite, enter an amorphous area, extend over into another crystallite, etc. Figure 1 is an idealized sketch of this situation.

(2) A second-order transition, characterized by a sudden change of quantities such as heat capacity and thermal expansion, takes place at lower temperatures than fusion, and presumably indicates that below this transition point the individual segments of the chain molecules do not carry out rotational and vibrational movements as a whole, but do carry out such internal Brownian movements above this point. Hence, according to the ideas of Eyring[9], Kuhn[21] and Meyer[25], they act as independent kinetic units of the system investigated. Figure 2 is an interpretation of this concept.

The crystallites of many high polymers, if irradiated with parallel monochromatic x-rays or electrons, produce diffraction patterns of a certain intensity and sharpness; these patterns, together with chemical evidence, allow deductions to be made as to the arrangement of the chains inside those crystallites and the arrangement of the atoms inside the chains. This kind of investigation has contributed greatly toward elucidating the structure of natural polymers, and has been recently applied with great success to longchain compounds, particularly by Fuller[11] and by Baker and coworkers.

Thus, crystallites are a useful tool for studying the fine structure and the texture of high polymers, but they also seem to be of considerable importance in their mechanical behavior. Experience shows that many processes, such as coagulation, swelling, quenching, annealing, stretching, or rolling of high polymers, are accompanied by either the production or disappearance of crystallites, and it was soon recognized that both types of phase transitions are intimately connected with the mechanism of the mechanical deformation of certain high polymers.

This paper discusses two of these connections—the influence of crystallization on the elastic behavior of rubber, and the influence of crystallization on reinforcement during plastic flow.

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CRYSTALLIZATION AND ELASTIC STRESS-STRAIN CURVE OF RUBBER

If one wishes to trace the influence of crystallization on the elastic behavior of high polymers, it seems appropriate to select natural rubber as the example. This substance is, perhaps, the most thoroughly investigated material among the long-chain polymers. Recently the lattice structure of the crystallized phase has been successfully investigated by Clark and coworkers[7], Gehman and Field[10, 13], Meyer and Lotmar[26], and Morss[27], with the result that the internal structure and the mutual arrangement of the chains are known with fair approximation. The diffraction pattern of the amorphous phase was thoroughly studied by Warren[31]; it indicates the presence of irregularly folded and coiled chains with internal *cis*-structure with respect to the existing double bonds.

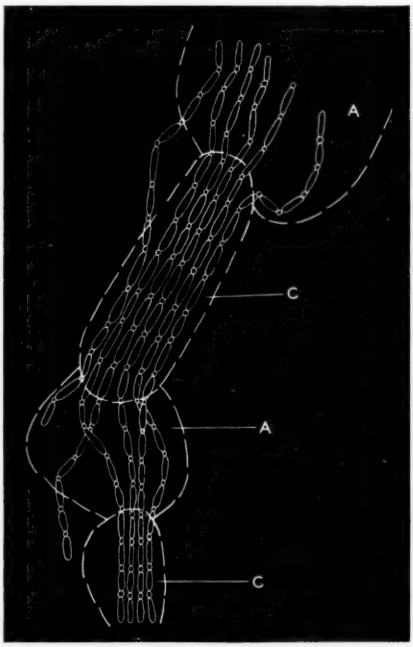


FIG. 1.—High polymer showing crystallized (*C*) and amorphous (*A*) areas.

Recently, Bekkedahl and Wood[2, 33] made a complete thermodynamic analysis of rubber by measuring the specific volume, energy, entropy, and heat capacities of the crystallized and amorphous phases as functions of temperature. This provides a valuable basis for any kind of theoretical consideration.

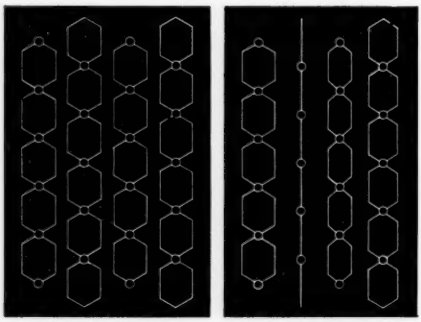
If slightly vulcanized rubber (0.5-1.0 per cent sulfur) is extended under normal conditions (20° C, final elongation around 700 per cent, rate of extension and relaxation around 100 per cent of the original length per minute), stress-strain curves of the general type shown in Figure 3 are obtained. The whole curve is inside the elastic limit; as soon as the stress is released, the sample returns to its initial state.

The first linear part of the curve (*OA*) corresponds to a modulus of elasticity between 10^6 and 10^7 dynes per sq. cm. It is due to a gradual uncurling and disentangling of the randomly coiled chain molecules, and can be interpreted on the

basis of the molecular theory of Mack[23] and the kinetic theory of long-chain elasticity[15, 21, 32]. X-Ray patterns prove that there is little or no crystallization during this period of extension.

The next part of the curve (*AB*) shows a distinct decrease of the elastic modulus down to 10^4 dynes per sq. cm.; this indicates that for some reason the material becomes more easily extensible than it was at the beginning of the experiment. It seems that some process is taking place inside the sample which supports the external force in producing the further extension of the specimen. This process is crystallization.

At the end of part *OA* some of the chains, or segments of them, have undergone considerable straightening and alignment, so that they now approach the arrangement they would possess if they were part of a crystallite. In this state they may be considered as a crystallization nucleus or center, and the van der Waals forces between them (although not particularly strong owing to the hydrocarbon nature of rubber) will suffice to overcome the small entropy loss involved and will force them into the crystal lattice. In so doing, these intermolecular



Chains without rotation. Chains with rotation.
FIG. 2.—Concept of internal rotation of chain molecules.

forces cause an additional straightening of the chains and produce an increase in length, dl, at constant external stress; this is analogous to the well-known action of the same intermolecular forces during the compression of a real gas, where they are responsible for the volume decrease, $-dV$, at constant external pressure in the van der Waals pressure-volume diagram. In both cases a first-order phase transition takes place; the gas condenses to a liquid, and the rubber crystallizes. In both cases latent heat is evolved—heat of condensation in the gas, heat of crystallization (about 4 calories per gram) in rubber.

Alfrey[1] recently developed a differential equation for the stress-strain curve of rubber which reflects the above consideration. Let us start with a 1-gram rubber sample of length l_0; let us extend it to length l, which is somewhere between *A* and *B* on Figure 3. To do this, we have to apply a certain stress σ; at the same time a certain amount of the material (q grams) has crystallized. If we produce an additional elongation of dl, we can either increase the stress by $d\sigma$ and keep q constant, or increase the amount of the crystallized phase by dq and keep σ constant.

In general, both parameters σ and q will change simultaneously, and we get the equation:

$$dl = \alpha d\sigma + \beta dq \qquad (1)$$

Quantities α and β contain the modulus of elasticity of the amorphous phase, the heat of crystallization, and the entropy difference between the amorphous and crystallized phase. Putting these magnitudes into Equation 1, Alfrey showed that the flat part of the stress-strain curve can be successfully described in range *AB*, and that reasonable agreement with the experiment can be obtained.

Beyond *B* the elastic modulus increases distinctly, and reaches rather high values (up to 10^{10} dynes per sq. cm.) in the neighborhood of end point *C* of the elastic extension curve. The reason is that the rubber crystallites have a much higher modulus (between 10^{10} and 10^{11} dynes per sq. cm.) than the amorphous phase and that, as soon as these crystallites predominate (q approaches unity), practically all the stress is taken up by the crystallized phase, and an additional elongation, *dl*, is now possible only by stetching the rather stiff and rigid crystals.

From this picture, some idea may be obtained of how to change the typical rubber extension curve of Figure 3 by designing a synthetic polymer appropriately. If we favor crystallization, either by increasing the forces between the chains (OH, CONH, CCl groups, etc.), or by making them fit more easily into

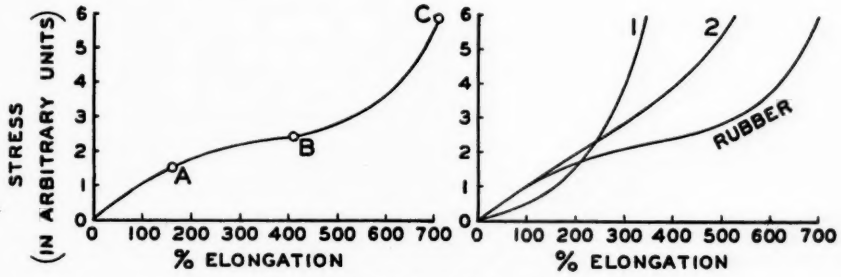


FIG. 3 (*Left*).—Typical stress-strain curve of rubber.
FIG. 4 (*Right*).—Theoretical stress-strain curves of high polymers.
1, crystallization favored; 2, crystallization prevented.

the lattice (straight, not too flexible chains), *OA* will be shortened and may disappear completely (curve 1, Figure 4), and the increase of the modulus will be comparatively rapid. If we prevent crystallizations (weak intermolecular forces, highly branched or substituted chains), there will be no flat part *AB* (Figure 3), and the curve will ultimately approach the shape of curve 2 in Figure 4.

As a matter of fact, extension of rubber at low temperatures (improved crystallization) approaches type 1, whereas high-temperature curves (inhibited crystallization) show a trend toward type 2.

It must be pointed out that this way of taking into account the influence of crystallization on the elastic behavior of long-chain polymers is still crude and preliminary; it will have to be improved before it can be considered a satisfactory description of the interaction of the external stress and the intermolecular forces.

INFLUENCE OF PHASE TRANSITIONS ON PLASTIC BEHAVIOR

If extended beyond their elastic limit, high polymers exhibit complicated behavior. If the temperature is not too high or too low and the rate of loading is moderate, three types of deformation are generally observed as soon as a stress or shear is applied: (1) An instantaneous deformation, which is partly or as a whole reversible after the external force is removed; (2) a subsequent slow deformation,

which slowly disappears partly or as a whole after the removal of the external influence; and (3) a permanent deformation, which does not disappear even after a long period.

To have a clear picture of prevailing conditions, it may be well to review briefly a few fundamental facts and definitions[4, 6, 19, 20, 24]. If a stress or shear is applied to a material such as platinum, quartz, glass, polystyrene, benzene, or water, two extreme cases of behavior are observed. In one, the external force produces a displacement, which disappears at once and completely as soon as the material is unloaded. Such a system is called an "elastic solid". Examples are platinum (and many other metals), quartz (and many other ionic crystals), diamond, etc. In the other extreme case, the external force produces a velocity gradient, which leads to a deformation through flow. This deformation stays on indefinitely after the force ceases to act. Such a system is called a "liquid". Examples are benzene, water, or mercury.

To represent these two cases simply, the deformation, D, of the sample can be measured (elongation of a filament, deformation of a compressed cylinder, etc.)

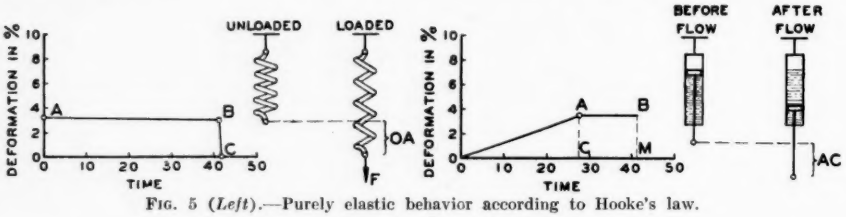


FIG. 5 (*Left*).—Purely elastic behavior according to Hooke's law.

$$D = OA = CB = F/E$$

where E = *modulus of elasticity.*

FIG. 6 (*Right*).—Purely liquid flow according to Newton's law.

$$D = \frac{\tau}{\eta} \cdot t.$$

where η = viscosity of liquid.
τ = external force (shear).
$D = AC = BM$.

and plotted against the time of observation. Figure 5 characterizes the elastic body. As soon as the stress or shear, F, is applied, deformation D takes place and remains constant as long as F acts. If F is removed, D disappears at once. Such a system may be conveniently idealized by a steel spring (Figure 5). Hooke found that, in many cases, D is proportional to F; the proportionality factor is the modulus of elasticity, E (or shear G) or Young's modulus, and we speak of an ideally elastic body or of a material obeying Hooke's law.

Figure 6 describes the behavior of a liquid. As soon as the external force (shear), τ, is applied, flow sets in, and deformation D increases proportional to time. If the flow is stopped by the removal of τ, D keeps its final value AC indefinitely. Such a system may be represented by a piston moving in a cylinder in which a liquid causes a certain friction (Figure 6). Newton found that frequently the velocity gradient of the flow is proportional to τ; we call the proportionality factor the "fluidity", its reciprocal the "viscosity" of the liquid, and speak of a Newtonian flow.

High polymers behave in almost all cases much less simply than elastic solids or liquids. To describe their properties, it seems convenient to build up, gradually, more and more complicated cases combining elastic elements as shown in Figure 5, and viscous elements as represented by Figure 6. This combination can

be made by arranging the elements in series or parallel. Maxwell[24] was the first to investigate such combinations. [If we arrange only elastic elements having different moduli in series, each of them is under the same stress and each extends according to $D_i = F/E_i$; E_i = modulus of element number i. Total elongation D is the sum of all D_i values. If the same elements are switched parallel, each of them attains the same elongation D, and the stresses F_i in the single elements are proportional to the E_i values. Such combinations, as well as the combination of only viscous elements, do not lead to systems approaching the behavior of high polymers.]

Figure 7 shows the arrangement in series. Both elements are subjected to the same stress; total deformation D is given by the addition of the individual deformations. If the load is applied, a sudden deformation D_0 takes place, the magnitude of which is given by the modulus of the elastic element. Then flow sets in and leads to an increase of D proportional to time according to the fluidity (or viscosity) of the plastic element. If the load is removed, the spring jumps back immediately from B to C, which is equal to OA, and the constant elongation CC' which was produced by the flow, stays indefinitely. The material shows plasto-elasticity.

Figure 8 shows the parallel arrangement of one plastic and one elastic element. Both elements have the same elongation at any time. In the first moment if the system is loaded, the two elements (which we assume to have the same cross-section) will have to stand the same stress. Under its influence, the spring starts to extend and the piston to flow. According to Hooke's law, the stress, which is taken up by the spring, increases proportionally to its elongation and, therefore, less and less force is left to move the piston. Finally all the stress is concentrated in the spring, and the piston stands still. The plastic element has gradually unloaded itself through flow and has shifted the stress to the spring, which at the end of the experiment bears the whole load. Under the simple conditions of our example, D increases exponentially with time (Figure 8), just as in the case of the monomolecular formation of a chemical compound or a radioactive element. If the load is removed, the elastic energy which is now stored in the extended spring begins to work and gradually moves the piston back to its original position, which, however, is reached only asymptotically. We have a retarded elastic recovery, and get a straight line for log D as a function of time, whose inclination is a measure for the retarding action due to the viscosity of the damping piston.

However, even the two composite systems of Figures 7 and 8 are not yet sufficient to represent the behavior of high polymers; but they are another step toward this goal. The flow curve of a typical high polymer (Figure 9) shows all the different elements of the two cases (Figure 7 and Figure 8) together—namely, a sudden jump, a retarded elastic extension, and a viscous flow.

The next approximation, therefore, leads to a system built up by two elastic and two plastic elements, having two different moduli, E_1 and E_2, and two different viscosities, η_1 and η_2, and being aranged parallel and in series, respectively. This case is shown in Figure 10; it has been frequently discussed in recent years, together with still more general systems by many authors, such as Bennewitz[5], Burgers[6], Holzmüller and Jenckel[18], Houwink[19], Leaderman[22] and others[5, 14, 17, 29, 30].

The application of an external force immediately produces an extension of the upper (isolated) spring, as shown by $OA = F/E_1$ in the curve of Figure 10, and the piston just below (isolated plastic element) starts into motion with a constant velocity τ/η_1. The other piston (coupled plastic element) also starts, at first

with velocity τ/η_2; but this velocity decreases asymptotically to zero because the stress is gradually transferred from the flowing piston to the extending spring. Reinforcement occurs along line AB. If at instant t the load is taken away, then the isolated elastic element contracts at once by the amount OA. This is represented in Figure 10 by the distance BC. The piston blow it does not move but stays where it was at instant t. The lower spring, however, starts contracting with a velocity that decreases to zero exponentially as a result of the damping action of the plastic element switched parallel. Thus the system approaches point M' asymptotically, and exhibits ideal and retarded elasticity back and forth, as well as true flow. The curve in Figure 10, which shows its behavior graphically, resembles fairly well the type of experimental curves represented in Figure 9; therefore, we may use it in making the next step of approximation in describing the deformation of high polymeric materials.

Presumably its molecular significance is that in such systems elastic elements, such as curled chain molecules or clusters of them (which exhibit kinetic elasticity

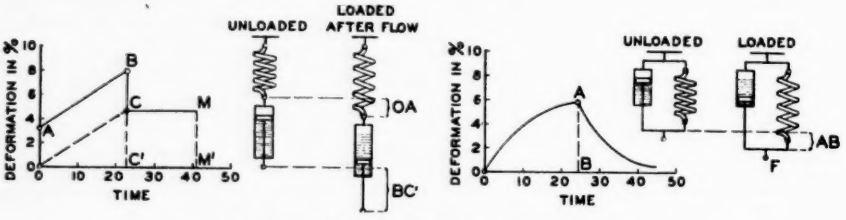


FIG. 7 (*Left*).—Elastic and plastic elements in series.

$D = D_0 + D_1 t.$
$OA = D_0 = F/E = BC =$ ideal elastic deformation.
$CC' = D_1 = \frac{\tau}{\eta} \cdot t = D_1 \cdot t = MM' =$ deformation due to flow.

FIG. 8 (*Right*).—Elastic and plastic elements in parallel.

$$D = F/E\left(1 - e^{-\frac{\tau}{\eta} t}\right) = D_2(1 - e^{-\lambda t}).$$

$E =$ elastic modulus of spring.
$\eta =$ viscosity of cylinder liquid.

or Mack elasticity), can be present in two different extreme situations: Either their extension does not involve the plastic displacement of any adjacent volume element, *e.g.*, orientation of a crystallite or flow inside of an amorphous area containing chain ends, or their extension is possible only if such a process of rearrangement takes place, since the elastic element is somehow connected with its surroundings (through-going chains, cross links, intermolecular forces, etc.).

Equally, two extreme types of viscous elements are possible. In one type the flow does not stress any elastic element in the immediate neighborhood (isolated plastic elements, which lead to flow), and in the other type they can flow only if any adjacent volume element is stressed and stores up elastic energy (combined plastic elements, which show retarded recovery).

In reality, all sorts of intermediate cases are to be expected; and instead of two moduli and two viscosities, a distribution curve of both will occur. Fuoss and Kirkwood[12] and Busse[8] showed that such distribution curves are needed to describe satisfactorily the electrical behavior of high polymers.

This brief paper, however, will discuss only the simplified case of Figure 10. The deformation as a function of time is then given by the simple equation:

$$D = D_0 + D_1 t + D_2(1 - e^{-\lambda t}) \qquad (2)$$

Here, D_0 represents the ideal elastic elongation, and D_1 accounts for the flow. These two characteristic constants (for the isolated elasticity and viscosity) can be directly and independently determined by measurements at very short times (such as sound velocity, rebound, etc.) and at very long times (linear flow after reinforcement). The rest of Equation 2 represents the exponential reinforcement.

The logarithm of $\gamma = D_0 + D_1 t + D_2 - D$ plotted against time gives a straight line,

$$\log \gamma = \log D_2 - \lambda t \tag{3}$$

whose intersect with the ordinate is ln D_2 while its slope is $-\lambda$. Thus these two constants (retarded modulus and retarding viscosity) can be determined by the evaluation of the logarithmic graph, which corresponds to Equation 3, provided the experimental values really lead to a straight line.

Recent experiments of M. Harris and J. Press have shown that in certain cases (proteins, cellulose esters, or polyesters at medium stresses) the above analysis leads to exponential reinforcement terms. Other systems, however, (viscose, rubber, or cellulose esters at high elongations) show a reinforcement which con-

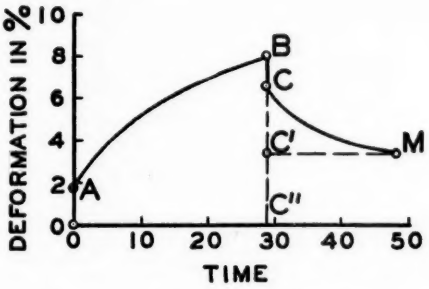


FIG. 9.—Flow curve of typical high polymer.

siderably exceeds the one predicted by relation 3. This is where crystallization seems to enter the picture.

The derivation of Equations 2 and 3 is based upon the assumption that a certain number of isolated and combined elastic and plastic elements are present at the beginning of the experiment, and that their quantity and quality do not change during the deformation of the sample. This seems to be true in some cases but not always. Systems which undergo phase transitions upon deformation will behave differently. In treating them we have to remember that during extension elastic elements may change into plastic ones, and therefore that retardation and reinforcement will exceed the amount predicted by the elementary unloading mechanism in Equation 2. Decrease of crystallinity by fusion or swelling has the opposite effect; it decreases the viscosities of the plastic elements, and facilitates the restoring and recovering action of the stressed elastic portions.

A simple way to find out the amount of such a reinforcement due to a phase transition is to measure the deviation of Equation 3 from a straight line in the logarithmic diagram. In fact, this equation sometimes leads to significant deviations which may be interpreted as being caused by additional crystallization. In doing so, however, one must keep in mind that this is not the only possible explanation for such a behavior of the material, because Equation 2 can be considered only as a rough approximation for the actual conditions. It contains only

two elastic and two plastic elements, while obviously a continuous distribution curve would be expected for both, and a more elaborate equation should be derived for the deformation of the sample as a function of time. Attempts in this direction have been undertaken[1], but the relations obtained have not yet been compared extensively with experimental data.

On the other hand are facts which may favor the explanation of the excess of reinforcement by additional crystallization. First is the fact that x-ray patterns indicate a decreased diffuse intensity and an increased intensity of the interference spots after plastic deformation of such systems as viscose or cellulose acetate. Furthermore, Hermans and Kratky[16], who studied the plastic deformation of cellulose xanthate, found that the amount and anisotropy of swelling are clearly affected by plastic deformation of the sample; and it is known generally that stretching decreases swelling and chemical reactivity.

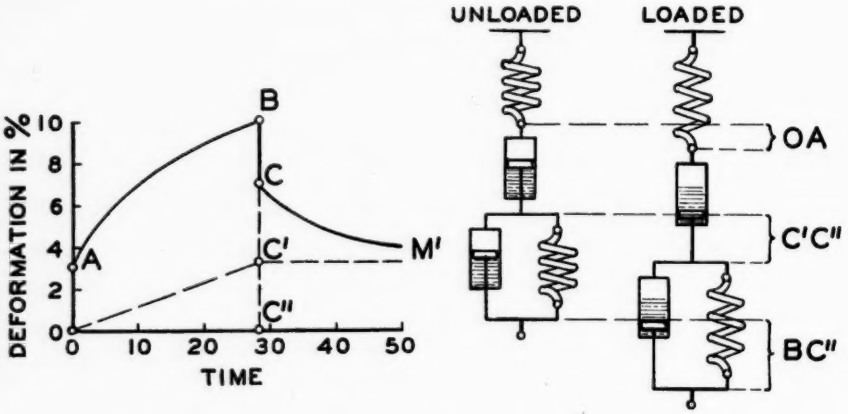


FIG. 10.—Elastic and plastic elements in series and in parallel combined.
$D = D_0 + D_1 t + D_2(1 - e^{-\lambda t})$.
$D_0 = OA = B$ = ideal elastic deformation.
$CC' = D_2(1 - e^{-\lambda t})$ = retarded elastic deformation.
$C'C'' = D_1 t$ = viscous flow.

Nevertheless, not enough experimental material is available to prove that the excess of reinforcement due to deformation in certain cases is due solely to phase transition. There is some indication that crystallization contributes to this effect, but further studies of flow curves and investigations of the extended samples with x-rays, by swelling experiments, or by the new method of Nickerson[28] will be necessary to clear the situation.

As to the second-order phase transition of high polymers, it seems that the freezing in of the internal Brownian movement is connected with the brittle point of the material. Particularly, polyhydrocarbons and polyesters show a distinct tendency to pass from a rubberlike state at higher temperatures to a brittle (glassy) state as soon as a certain rather sharp temperature limit is reached. Bekkedahl and Wood[2, 33] determined this transition point for rubber to be −80° C.; others[3, 18, 19] found that the brittle point of polystyrene is around +80° C. The paper of Carswell, Hayes, and Nason (page 639) gives additional convincing experimental evidence of this point.

Summarizing, our present experimental knowledge suggests a distinct influence

of both types of phase transitions on the mechanical behavior of high polymers, although it is not yet possible to connect quantitatively the amount of converted material with the magnitude of the mechanical effect.

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A STATISTICAL TREATMENT OF CRYSTALLIZATION PHENOMENA IN HIGH POLYMERS *

T. ALFREY and H. MARK

DEPARTMENT OF CHEMISTRY, BROOKLYN POLYTECHNIC INSTITUTE, BROOKLYN, NEW YORK

INTRODUCTION

It has been emphasized, particularly by Kauzmann and Eyring[1], that the kinetic units of high polymers are best considered to be segments, rather than whole molecules. Kistler[2] has recently given a satisfactory description of the plastic properties of high polymers on this basis. It seems probable that segments, rather than whole molecules, also are the structural units of high-polymer crystallites. A single molecule may extend through several crystalline and several amorphous areas. As a result, certain familiar characteristics of phase equilibria of low molecular-weight materials do not appear in the crystallization of high polymers. This paper will attempt to explain the anomalous aspects of high-polymer crystallization on the basis of free-energy changes in the amorphous segments.

The crystallization of rubber and other elastomers during extension is an important example[3, 4]. The stress-strain curve of rubber (Figure 1) may be divided conveniently into three sections. During the first 100 to 200 per cent elongation, sometimes called the range of "gaslike" elasticity, the free-energy change is due almost entirely to entropy changes[5]. In the middle region, the hydrocarbon chains have been straightened out to such an extent that the intermolecular forces are able to cause crystallization. This crystallization process acts to aid the external stress and to cause additional elongation. In this region, a small added stress results in a large additional elongation, and the free-energy change associated with stretching includes both energy and entropy terms. In the third section, the process of crystallization is practically finished, and the rubber exhibits pure "crystal" elasticity.

STRESS-STRAIN CURVE OF RUBBER

The process of stretching rubber involves the straightening of individual polyisoprene chains from somewhat curled or kinky configurations into more extended shapes. The resistance offered to this process is due not to internal orienting forces, but rather to the statistical predominance of partially curled configurations. A long hydrocarbon chain is unlikely to be either very tightly curled or completely straight. This is shown in Figure 2, where W, the probability of a chain of n links having its two ends separated by a distance r, is plotted as a function of r. Different authors[5, 6] proposed the function:

$$W = C \cdot \frac{1}{n^{3/2}} \cdot e^{\left(-\frac{3r^2}{2nl_a^2}\right)} r^2 \qquad (1)$$

* Reprinted from *The Journal of Physical Chemistry*, Vol. 46, No. 1, pages 112-118, January 1942. This paper was presented at the Eighteenth Colloid Symposium, Cornell University, Ithaca, N. Y., June 19-21, 1941. The first author is Monsanto Chemical Company Research Fellow at the Polytechnic Institute of Brooklyn.

If the configurational entropy is taken as $k \ln W$, and the internal energy is considered to be unaffected by extension, it is possible to calculate the free energy of rubber as a function of temperature and extension. Such a calculation leads to the correct order of magnitude for the coefficient of elasticity, and successfully predicts the thermoelastic properties of rubber in the range where no crystallization takes place.

As an extension of this theory into the range of crystallization, the following differential stress-strain curve has been suggested:

$$d\gamma = \frac{1}{K}(1-q)\,dS + \alpha\,dq + \frac{1}{K'}\,q\,dS \qquad (2)$$

Here q is the fraction crystallized, γ is the elongation, S is the stress, and K and K' are the elastic coefficients of the amorphous and crystalline phases, respectively. $\alpha\,dq$ represents the additional elongation caused by the process of crystallization. This formula merely indicates that an increase in stress, dS, results in an increment in length, $d\gamma$, made up of an elongation due to the elastic stretch-

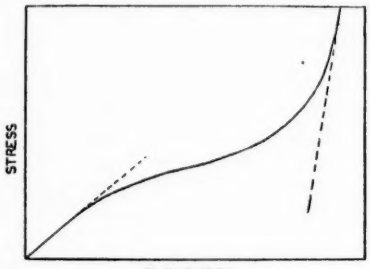

FIG. 1.

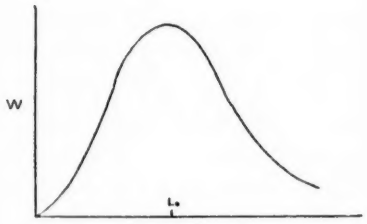

FIG. 2.

FIG. 1.—Stress-strain curve of rubber.
FIG. 2.—Probability, W, of the two ends of a polyisoprene chain being separated by a distance L.

ing of the amorphous material, plus an additional elongation due to the process of crystallization caused by the added stress, plus a very small elastic elongation of the crystalline material. This formula is probably an oversimplification of the problem, since it assumes that the amorphous and crystalline elastic elements are joined in series, whereas there is no reason to expect this to be exactly true. However, when an empirical relation between q and γ (from observed x-ray data) is substituted in this formula, a stress-strain curve of the proper general shape is obtained. A more complete theory should predict the amount of crystallization, q, as a function of S or γ, as well as the effect of crystallization on the stress-strain curve.

EFFECT OF TEMPERATURE AND ELONGATION ON CRYSTAL-AMORPHOUS EQUILIBRIUM OF HIGH POLYMERS

The free energy of an amorphous high polymer, which is important in determining the nature of the amorphous-crystalline equilibrium, depends not only on the temperature and pressure, but also on the tension. The process of crystallization itself may result in a constriction or a relaxation of the intermicellar amorphous segments, and hence in a free-energy change of the amorphous phase. Such free-energy changes may be advanced as the explanation of

the unsharp melting point of rubber crystallites, the dependence of crystalline content on degree of extension, etc.

Figure 3 represents an extremely oversimplified model of a crystallizing high polymer. On the basis of this model, a qualitative prediction can be made of the thermoelastic behavior of rubber in temperature and extension ranges where the crystallization process takes place.

Consider a segment of a hydrocarbon molecule, both ends of which are in crystalline areas (Figure 3):

N = number of monomer units in the segment considered

q = fraction of segment in crystalline phase

D = total distance between ends of segment

$(1-q)$ = fraction in amorphous phase

Nq = number of units in crystalline phase

$N(1-q)$ = number of units in amorphous phase

l = length along chain of a crystallized monomer unit

$L = D - nql$ = distance between ends of amorphous chain

The condition for equilibrium between the amorphous and the crystalline phases is that the free energy of the whole system must be a minimum. Now the entropy of an amorphous hydrocarbon chain depends on both the number of monomer units and the total distance between the ends. Here the number of monomer units in the amorphous chain is $N(1-q)$, and the distance between the ends is $(D-nql)$. The free energy of the entire segment under consideration is, therefore, given by the following expression:

$$F(D, T, q) = NH_0 + Nq\Delta H - T\left[NqS_{\text{cryst.}} + S \right. \tag{3}$$

where

H_0 = enthalpy of amorphous rubber

ΔH = enthalpy change, per monomer unit, on crystallization

$S_{\text{cryst.}}$ = entropy per monomer unit in crystal

$S_{D-Nql}^{N(1-q)}$ = entropy of an amorphous hydrocarbon chain of $N(1-q)$ units and length $(D-Nql)$

The equilibrium value of q for any given D and T is obtained by setting $\Delta F/\Delta q = 0$. This results in the expression:

$$0 = \Delta H - T\left[\Delta S_0 + \frac{1}{N} S_{\text{max.}}^{N} - S_{D-Nql}^{N(1-q)} + S_{D-Nql-l}^{N(1-q)-1}\right] \tag{4}$$

where

ΔS_0 = entropy of crystallization from unstressed amorphous phase

$S_{\text{max.}}^{N}$ = entropy of a chain of N units (unstressed)

$S_{D-Nql}^{N(1-q)}$ = entropy of chain of $N(1-q)$ units and length $(D-Nql)$

$S_{D-Nql-l}^{N(1-q)-1}$ = entropy of above chain after one unit has crystallized, leaving one less unit in the chain and a length shorter by l

The probability, W, that the distance between the two ends of the amorphous segment corresponds to a given value of L should be a function of the general type plotted in Figure 2. If we use for W the Expression 1 of Guth and Mark, and let $S=k \ln W$, we obtain the following expression for the entropy of an amorphous chain:

$$S=k \ln C-\frac{3}{2} k \ln n-\frac{3kr^2}{2nl_a^2}+2k \ln r$$

This expression for W is not rigorously applicable to the model under consideration, since several of the assumptions made in its derivation cannot hold here. The most satisfactory approach to the configurational entropy of long-chain molecules has been made recently by Huggins[7]. However, Equation 1 expresses the one salient characteristic of our model amorphous segment—the maximum probability of some intermediate value of L. Substituting this into Equation 4, we obtain:

$$0=\Delta H-T\Delta S_0-\frac{T}{N} S^N_{\text{max.}} \frac{3}{2} kT \ln \frac{N(1-q)}{N(1-q)-1}-\frac{3}{2} kT \frac{(D-Nql)^2}{(N)(1-q)l_a^2}$$
$$+\frac{3}{2} kT \frac{(D-Nql-l)^2}{l_a^2 \cdot [N(1-q)-1]}+2kT \ln \frac{(D-nql)}{(D-nql-l)} \qquad (5)$$

This can be solved for T more conveniently than for q.

$$\frac{1}{T}=\frac{1}{\Delta H}\left[\Delta S_0+\frac{1}{N} S^N_{\text{max.}}+\frac{3}{2} k \ln\left(\frac{N(1-q)}{N(1-q)-1}\right)+\frac{3}{2} k \frac{(D-Nql)^2}{N(1-q)l_a^2}\right.$$
$$\left.-\frac{3}{2} k \frac{(D-Nql-l)^2}{[N(1-q)+1]l_a^2}-2k \ln \frac{D-Nql}{D-Nql-l}\right] \qquad (6)$$

We now have an expression for T, the temperature of equilibrium, as a function of N, D, and q. The quantities ΔH and ΔS_0 can be evaluated from the experimental data of Bekkedahl and Wood[8]. Using this model, we may now discuss the crystallization of rubber under various conditions.

MELTING POINT OF UNSTRETCHED RUBBER

At the beginning of the crystallization of unstretched rubber, the intermicellar amorphous segments are in an unstressed condition. On the average, they may be considered to have the most probable lengths for their numbers of monomer units. This corresponds to a position near the maximum of the probability curve, in Figure 2. As crystallization proceeds, the chains are forced into less favorable configurations, *i.e.*, to the left of the maximum of Figure 2. Growth of the crystal micelles results in a reduction both in the length, L, and the number of units, n, in the amorphous segment. However, L decreases more rapidly relatively than does n (see Figure 4). When a unit enters the crystal lattice, there is not only an entropy decrease owing to the immobilization of the entering unit itself, but also an entropy loss owing to the constriction of the amorphous chain. As a result, while ΔH remains the same for each crystallizing unit, ΔS becomes greater for the later units. There is no sharp melting point, but rather a melting range.

CRYSTALLIZATION OF STRETCHED RUBBER

At the beginning of the crystallization of stretched rubber, the intermicellar chains are held in configurations of low probability—to the right of the maximum of Figure 2. The process of crystallization releases the tension on the amorphous segment, and allows it to take on configurations nearer to that of maximum probability (see Figure 4). Thus the entropy changes in the intermicellar chains here aid rather than hinder the process of crystallization. The entropy decrease accompanying the loss in mobility of the entering monomer unit is somewhat offset by the entropy increase of the amorphous chain. Equation 6 predicts an unsharp melting point, just as in the case of unstretched rubber, but for any given degree of crystallization, q, the equilibrium temperature is higher in the case of stretched rubber[4, 9].

SPONTANEOUS EXTENSION

An important prediction of the gaslike theory of rubber elasticity was the increase of K with temperature. The model discussed in this paper leads to the

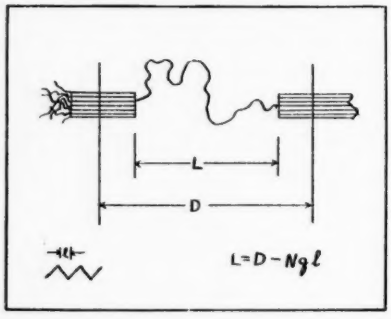

FIG. 3.

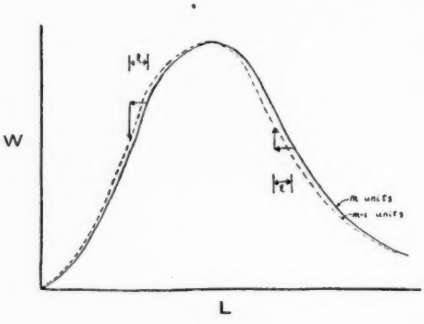

FIG. 4.

FIG. 3.—Simplified picture of crystallizing rubber.
FIG. 4.—Effect of crystallization of one monomer unit upon the length and configurational probability of the intermicellar amorphous chain.

expectation of much more complex thermoelastic properties in the range of crystallization than in the range of gaslike elasticity. The phenomenon of spontaneous extension, for example, is readily explained on this basis. If the model system in Figure 3 is extended to a distance D such that a small amount (say 10 per cent) of crystallization takes place, the intermicellar segment is constrained in a "stretched" state, *i.e.*, to the right of the maximum in Figure 2. This means that the macroscopic rubber sample is under tension. If the sample is now cooled, holding D constant, further crystallization takes place. The amorphous segment becomes less constrained, *i.e.*, moved to more and more probable values of L. This means that the tension of the sample becomes less and less. If the crystallization by cooling is carried far enough, the amorphous segment is shortened beyond its most probable length. The specimen is now under compression in the direction of orientation, rather than tension. If released, it does not contract but extends spontaneously. Exactly this phenomenon has been observed experimentally in the cases of rubber[10] and cellulose acetate[11].

SUMMARY

An attempt has been made to explain the anomalous crystallization behavior of high polymeric materials on the basis of entropy changes in the amorphous material. The free energy of the amorphous phase depends not only on the temperature and pressure, but also on the degree of extension and the fraction of crystalline material in the sample. A crude model embodying these characteristics was proposed. On the basis of this model, it is possible to explain the unsharp melting point of rubber, the dependence of crystallization on the degree of extension, and the phenomenon of spontaneous extension.

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STATISTICAL THERMODYNAMICS OF RUBBER *

FREDERICK T. WALL

NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

INTRODUCTION

It has been proposed that when a piece of unvulcanized rubber is stretched, the forces involved arise principally from straightening the long rubber molecules rather than from intermolecular attractions or from deformation of chemical bonds and bond angles[1]. Assuming free rotation is possible about the various bonds of a long molecule, it is recognized that such a molecule can assume any of a great many configurations when left to itself. It is improbable, however, that a molecule will be found in a straightened condition[2], because only a few configurations are compatible with such a condition. By associating the idea of configuration probability with entropy, it becomes possible to calculate some thermodynamic properties of rubber.

Several investigators, including Guth and Mark[3], Kuhn[4], and Pelzer[5] have contributed to the statistical theory of rubber. Although these workers took cognizance of the statistical nature of the problem, some parts of their treatments require modification. Their procedure consisted essentially of calculating the entropy of a single molecule, then relating the changes taking place in that molecule to the macroscopic behavior of rubber. In the treatment which follows here, no attempt will be made to calculate individual molecular entropies but, instead, the system will be considered in its entirety. At the same time the macroscopic behavior of the rubber will be related statistically to the individual molecules in a plausible way.

THEORETICAL CALCULATIONS

Let us assume that the piece of rubber we are dealing with has the shape of a cylinder with cross-sectional area A and length l_0 in its unstretched condition. When the rubber is at its equilibrium length, the individual molecules will have various shapes and orientations, such as are illustrated in Figure 1. Let x equal the component of the distance between the ends of a given molecule along the direction in which stretching takes place. It is then clear that the probability of

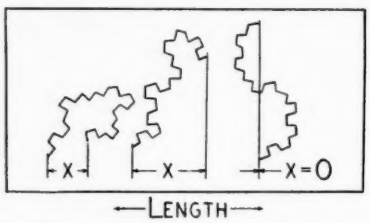

FIG. 1.—Plane projections for rubberlike molecules.

* Reprinted from *The Journal of Physical Chemistry*, Vol. 10, No. 2, pages 132-134, February 1942.

a given molecule having a value of x in the range x to $x+dx$ will be given by the normal probability distribution function:

$$p(x)dx = \frac{\beta}{\sqrt{\pi}} \exp(-\beta^2 x^2)dx. \tag{1}$$

In this expression, β is a constant which depends on the number of units in the molecule chain and the length of each unit. Equation (1) is valid, of course, only if the chains are uniformly long; for large values of x it is subject to the usual limitations encountered in problems of this type[6]. A graph of $p(x)$ plotted against x appears as curve S in Figure 2.

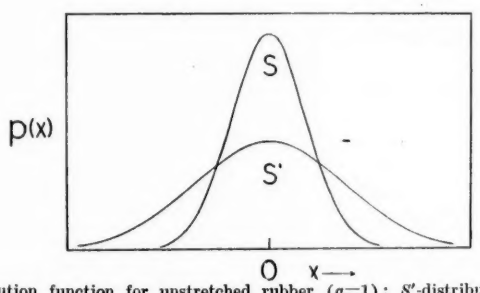

FIG 2.—S-distribution function for unstretched rubber ($\alpha=1$); S'-distribution function for stretched rubber with 100 per cent elongation ($\alpha=2$).

Now let the macroscopic piece of rubber be stretched from length l_0 to l. It is then reasonable to suppose that all of the x's will change in the same ratio[7] as the overall length, giving rise to the distribution curve S' of Figure 2. If $\alpha=l/l_0$, then the new distribution will be given by:

$$p'(x)dx = \frac{\beta}{\alpha\sqrt{\pi}} \exp(-\beta^2 x^2/\alpha^2)dx. \tag{2}$$

If S corresponds to the most probable (equilibrium) distribution, then S' will have a lower probability, meaning that the stretched rubber will have a lower entropy. Our problem then resolves itself into calculating the relative probabilities of finding the system in the states S and S'.

Let us divide the x space into a number of cells, the ith of which is located in the neighborhood of x_i and has the size Δx_i. Also let p_i be the probability that a given molecule will be in the ith cell and let s_i be the number of molecules in that cell. Then the probability P of finding the system characterized by s_1, s_2, s_3, ... etc. will be given by:

$$P = N! \prod_i p_i^{s_i}/s_i! \tag{3}$$

where N is the total number of molecules. The probability P_0 of finding molecules in their most probable distribution will be:

$$P_0 = N! \prod p_i^{n_i}/n_i!, \tag{4}$$

where $n_i = Np_i$. The ratio of the two probabilities will then be:

$$\frac{P}{P_0} = \prod_i \frac{n_i!}{s_i!} p_i^{s_i - n_i}. \tag{5}$$

Introducing Stirling's approximation, $n! = (n/e)^n$, it is found on simplification that:

$$\frac{P}{P_0} = \prod_i \left(\frac{n_i}{s_i}\right)^{s_i} \tag{6}$$

or

$$\ln \frac{P}{P_0} = \sum_i s_i \ln \frac{n_i}{s_i}. \tag{7}$$

But if P and P_0 refer, respectively, to the states S' and S represented in Figure 2, then it follows by Equations (1) and (2) that:

$$n_i = \frac{N\beta}{\sqrt{\pi}} \exp(-\beta^2 x_i^2)\Delta x_i \tag{8}$$

and

$$s_i = \frac{N\beta}{\alpha\sqrt{\pi}} \exp(-\beta^2 x_i^2/\alpha^2)\Delta x_i. \tag{9}$$

Hence

$$\frac{n_i}{s_i} = \alpha \exp[-\beta^2 x_i^2(\alpha^2-1)/\alpha^2] \tag{10}$$

and

$$\ln \frac{P}{P_0} = \sum_i s_i \ln \alpha - \frac{\beta^2(\alpha^2-1)}{\alpha^2} \sum_i s_i x_i^2. \tag{11}$$

But $\sum_i s_i = N$ and $\sum_i s_i x_i^2 = N\overline{x^2}$, where $\overline{x^2}$ is the average value of x^2 for the distribution S'. By use of Equation (2), it is found that $\overline{x^2} = \alpha^2/2\beta^2$. Therefore:

$$\ln \frac{P}{P_0} = N \ln \alpha - N(\alpha^2-1)/2 \tag{12}$$

or

$$P = P_0 \alpha^N \exp[-N(\alpha^2-1)/2]. \tag{13}$$

It can readily be established from Equation (13) that P has its maximum value (equal to P_0) when $\alpha = 1$, thus providing a check on the work so far.

The entropy change on stretching can now be calculated immediately. Evidently:

$$S - S_0 = k \ln \frac{P}{P_0} = Nk \ln \alpha - Nk(\alpha^2-1)/2. \tag{14}$$

Replacing α by l/l_0 and differentiating, it is found that:

$$\left(\frac{\partial S}{\partial l}\right)_E = -\frac{Nk}{l_0}\left(\frac{l}{l_0} - \frac{l_0}{l}\right). \tag{15}$$

The partial derivative in Equation (15) is taken to be at constant energy (E), because only free rotation effects have been utilized. But from thermodynamics we know that:

$$dE = TdS + rdl \tag{16}$$

where τ is the tension in the rubber. Accordingly:

$$\tau = -T\left(\frac{\partial S}{\partial l}\right)_E = \frac{NkT}{l_0}\left(\frac{l}{l_0} - \frac{l_0}{l}\right). \tag{17}$$

If ρ is the density of the rubber in its unstretched condition and M the molecular weight, it follows that:

$$\tau = \frac{\rho ART}{M}\left(\frac{l}{l_0} - \frac{l_0}{l}\right). \tag{18}$$

From this we deduce the elastic constant or Young's modulus to be:

$$\varepsilon = \frac{\rho RT(l+l_0)}{Ml} \approx \frac{2\rho RT}{M}. \tag{19}$$

The approximate form of Equation (19) holds for small relative stretchings, but it is interesting to note that the more exact form does not predict a constant value for the elastic constant. Assuming $\rho = 1$ g/cm^3, $T = 300°$K and $\varepsilon = 10^6$ dynes per sq. cm., M is calculated to be about 50,000. This value for the molecular weight is not unreasonable, for it would imply that the molecules consist of approximately 730 isoprene units, which is the correct order of magnitude.

DISCUSSION

The principal difference between the present calculation and previous ones lies in the manner of relating the macroscopic stretching to the straightening of the individual molecules. The fact that not all the molecules undergo the same displacement is automatically taken care of in the present treatment, and no uncertain assumptions relative to this fact are necessary. The final results of the calculations do not involve individual bond lengths or bond angles, but depend only on the molecular weight and on externally measurable physical properties.

The dependence of τ on l as shown in Equation (18) is the same as in an equation derived by Pelzer[5], but with a different coefficient. Pelzer showed that this dependence is in better agreement with experiment than is an equation with τ directly proportional to $l - l_0$. The tension is found, as before, to be proportional to the absolute temperature, a point which has been verified experimentally by Meyer and Ferri[8].

The theory here developed is not limited to the stretching of rubber, but can be applied equally well to compression. It will be seen that Equation (18) has the proper limiting behavior as l approaches zero. A formula which predicts τ to be proportional to $l - l_0$ obviously would fail for compression. It is accordingly recommended that the equation of state for an ideal piece of rubber be taken as $\tau = \text{const. } T(l/l_0 - l_0/l)$, instead of $\tau = \text{const. } T(l - l_0)$, even if the latter is a little simpler.

In view of the assumptions made, the theory cannot be expected to hold well for all polymeric substances, since no account is taken of intermolecular forces or of deformations other than free rotation effects. The fact that rubber has such a large extensibility makes the picture assumed here appear valid when applied to that substance. Other polymeric substances which exhibit extensibility to a much lesser extent are more or less in crystalline form, with the various chains bearing ordered relationships to each other. Rubberlike substances are in a class by themselves, and cannot be regarded as (crystalline) solids.

SUMMARY

The entropy change for the stretching of rubber is calculated by statistical methods, neglecting intermolecular attractions and deformation of bonds and bond angles. The calculation involves the probability of finding the system with a given

distribution of molecular configurations. An equation of state relating the tension, length, and temperature of a rubber band is then derived. Following this a discussion of the applicability and the limitations of the theory is presented.

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DETERMINATION OF THE MOLECULAR WEIGHTS AND THE STRUCTURES OF RUBBER, GUTTA-PERCHA AND BALATA

COMMUNICATION NO. 258 ON MACROMOLECULAR COMPOUNDS

COMMUNICATION NO. 49 ON ISOPRENE AND RUBBER *

H. STAUDINGER and KL. FISCHER

DEPARTMENT OF RESEARCH ON MACROMOLECULAR CHEMISTRY, CHEMICAL LABORATORY, UNIVERSITY OF FREIBURG I. BR., GERMANY

THE MACROMOLECULAR STRUCTURE OF RUBBER, GUTTA-PERCHA AND BALATA

The method used to determine the constitutions of rubber, gutta-percha and balata is essentially the same as that used for organic substances of low molecular weights, *i.e.*, the substance is dissolved in a solvent, and the size and character of the particles in solution are determined[1]. For a long time the nature of colloidal solutions of these hydrocarbons was in dispute. Up to twenty years ago, it was commonly assumed that the molecules of these hydrocarbons are relatively small, and that their colloidal particles are formed by the assemblage of small molecules into micelles through the agency of secondary forces. It seemed to Pummerer, Nielsen and Gündel[2] that in certain solvents, such as camphor and menthol, rubber is dissolved in a low-molecular state. Subsequently, however, this observation was proved to be incorrect[3].

According to the opinion of Meyer and Mark[4], colloidal particles of rubber are composed of relatively long primary-valence chains, which contain from 75-150 isoprene residues. These chains are, in turn, assembled into micelles by "micellar forces." The authors explain this in the following way: "The high viscosity of rubber solutions, *e.g.*, in benzene, would lead one to conclude that very large, highly solvated micelles are present in these solvents." At the time, this hypothesis seemed to explain quite satisfactorily the nature of rubber and its solutions, for the great tendency of these solutions to undergo certain changes on standing, which are manifest by an increase or decrease in viscosity, is readily comprehensible on this basis.

Contrary to this view, Staudinger and Fritschi[5] came to the conclusion that rubber is composed of macromolecules, that its colloidal particles in dilute solutions are "macromolecules," and, consequently, that chemical reduction of these macromolecules yields a high-molecular hydrorubber. The colloidal solutions

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Journal für Praktische Chemie*, Vol. 157, Nos. 1-3, pages 19-88, December 24, 1940. This paper represents the Thesis of Kl. Fischer at Freiburg i. Br., 1938. For the 257th Communication on Macromolecular Compounds, see Staudinger, *Zeitschrift für Physikalische Chemie*, Vol. 47, Part B, p. 155 (1940), which is also the 49th Communication on Isoprene and Rubber. For the 48th Communication on Isoprene and Rubber, see Staudinger, *Proceedings of the Rubber Technology Conference*, London, 1938, p. 253; RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 12, No. 2, p. 117 (April 1939).

themselves are stable, and show no aging phenomena[6]. Accordingly the aging phenomena manifested by rubber are to be attributed to the reactivity of its unsaturated hydrocarbon. But even this does not lead to any definite proof of the validity of the micellar concept of Meyer and Mark or of the macromolecular concept. The macromolecular structure of colloidal particles has been verified by the transformation, by reduction, of a series of homologous polymeric polyprenes into the corresponding series of polymeric polypranes[7], for it is impossible to reconcile such a transformation with the view, accepted so widely up to that time[8], that rubber particles have a micellar structure.

In carrying out such polymeric transformations, difficulties were encountered with rubber because of its reactivity, especially its sensitivity to oxygen. When a terpene of the composition, $C_{10}H_{16}$, is reduced to a saturated hydrocarbon, $C_{10}H_{20}$, reduction continues practically to completion, despite the fact that a small percentage of the unsaturated terpene is autoöxidized by atmospheric oxygen. For the presence of a very small quantity of oxygen, *e.g.*, 0.047 per cent, is sufficient to oxidize only 0.2 per cent of the terpene, if it is assumed that one mol of oxygen reacts with one mol of terpene and that all oxygen takes part in the reaction. This small percentage of autoöxidation products need not ordinarily

TABLE I

DEGRADATION OF HOMOLOGOUS POLYMERIC RUBBER HYDROCARBONS BY OXYGEN IN EQUIMOLECULAR PROPORTIONS

Product	Molecular weight	Percentage of oxygen
$(C_5H_8)_{10}$	680	4.7
$(C_5H_8)_{100}$	6,800	0.47
$(C_5H_8)_{1000}$	68,000	0.047
$(C_5H_8)_{5000}$	340,000	0.0094

cause any concern, because, in purifying the reduction product, *e.g.*, by distillation, they remain behind as small quantities of greaselike substances which can easily be eliminated.

If rubber with an average degree of polymerization of 1000 is transformed in the same way into a hydrorubber, this 0.047 per cent of oxygen is sufficient to break down the complete system of macromolecules of this high-molecular rubber. Here too, it is assumed that one molecule of oxygen reacts with one macromolecule of rubber, and that all oxygen is consumed.

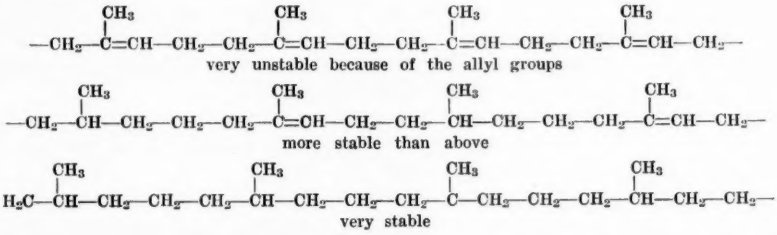
The oxidation products of rubber consist of fragments of macromolecules and are, therefore, degraded rubbers. They cannot be removed, or can be only incompletely removed, from the unaltered hydrorubber. Accordingly if, in the reduction process, oxygen is not rigorously excluded, it is quite impossible to transform rubber of a definite average degree of polymerization into an analogous reduction product of the same degree of polymerization[9]. Ordinarily, therefore, when rubber is reduced to a hydrorubber, a product with a lower average degree of polymerization than the degree of polymerization of the original rubber is obtained.

The small percentages of oxygen which are necessary to bring about the autoöxidation of polyprenes of different average degrees of polymerization[10] are shown in Table I. In this case too, it is assumed that one molecule of oxygen reacts with one molecule of polyprene[11].

In transforming polyprenes into polymerically analogous polypranes, difficulty is encountered not only because polyprenes are degraded by oxidation, but also

because the allyl groups make these unsaturated hydrocarbons very unstable[12]. Consequently precautions must be taken in this reduction so that, at the beginning, some of the double bonds of the polyprene are reduced at a relatively low temperature (100-120° C). The resulting partially unsaturated products are much more stable than the original polyprenes themselves, and are more difficult to crack, since the allyl groups, to which the ease of cracking is attributable, are eliminated.

The reduction can then be completed as a second step at a higher temperature (150-160° C). As has been pointed out several times in the past[13], the resulting hydrorubber is very stable, and cannot be cracked, even at very high temperatures.



In demonstrating the macromolecular structure of rubber, gutta-percha and balata, not only was each one of these substances transformed into its corresponding polymeric hydrogenation product, but into a series of products of different average degrees of polymerization[14]. In an earlier work[15], evidence of the transformation of polyprenes into the corresponding polymeric polypranes was obtained by determining the visocities of solutions of the sols of the original unsaturated hydrocarbons and of their hydrogenation products, and calculating the η_{sp}/c values from these measurements.

The η_{sp}/c values of the original polyprenes were approximately the same as those of their hydrogenation products. From this it was concluded that these hydrogenation products have the same average degrees of polymerization as the original polyprenes and, therefore, that reduction of polyprenes leads to the corresponding polymeric polypranes. This conclusion seemed warranted in view of the fact that squalene and hydrosqualene have the same η_{sp}/c values[16]. Furthermore, hemicolloidal polyprenes have the same K_m values as those of hemicolloidal polypranes[17]. The double bonds in the fibre molecules of these hydrocarbons have, therefore, no influence on the magnitudes of the η_{sp}/c values, and the latter depend only on the length of the molecules.

In earlier publications[18], data on the average degrees of polymerization and average molecular weights of polyprenes and polypranes were reported. These data were not, however, obtained by the osmotic method, but were calculated from η_{sp}/c values. It was assumed in these calculations that the K_m constants of hemicolloidal polyprenes and polypranes can be used for calculating the molecular weights of mesocolloidal and eucolloidal members. Hence it was assumed also that the following viscosity law of fibre molecules is valid for all members of an homologous polymeric series:

$$\frac{\eta_{sp}}{c_{gm}} = K_m M \tag{1a}$$

$$\frac{\eta_{sp}}{c} = K_m P \tag{1b}$$

where M is the molecular weight, P the degree of polymerization, η_{sp} the specific viscosity, c_{gm} the concentration (in grams per liter), and K_m a constant. The expression: η_{sp}/c, is designated in the following pages as the viscosity number[19].

Formulas (1a) and (1b) can be written also in the following form:

$$\frac{\eta_{sp}}{c} = K_{equiv.} \cdot n \tag{1c}$$

where n is the number of chain-members, and $K_{equiv.}$ is the chain equivalent weight constant. The latter is equivalent to the K_m constant divided by the number of chain members in the base molecule.

In the light of later investigations, this assumption is not correct, for the above relation does not hold true of mesocolloidal and eucolloidal polyprenes and polypranes, and the experimental K_m values of hemicolloidal members cannot be used for calculating the molecular weights of high-molecular members. According to recent determinations, the K_m constants of high-molecular polyprenes and polypranes have an average value of 1.4×10^{-4}.

To obtain an idea of the average degree of polymerization of polyprenes and of the corresponding polypranes concerned in the new investigation, this new K_m value was used for calculating the degrees of polymerization of both substances. Table II summarizes the experimental results obtained in the earlier investigation and in a series of new experiments.

The experimental values recorded in Table 2 furnish proof of the macromolecular structure of polyprenes in general and, therefore, of rubber, guttapercha and balata in particular. With this as a starting point, further research on these products can be carried out in a reliable way.

FORMER DETERMINATIONS OF THE MOLECULAR WEIGHTS OF VARIOUS RUBBERS

The weights of the individual colloidal particles in rubber solutions have been determined by means of osmotic measurements by various investigators. More recently they have been determined also by measurements with ultracentrifuges. Since it has now been proved that rubber has a macromolecular structure, such determinations give the molecular weights and not the weights of micelles[24], as had previously been assumed[25].

In determining the molecular weight of rubber by osmotic measurements, a difficulty is encountered in that the p/c values increase with increase in concentration, and therefore the van't Hoff law is not valid for these solutions as it is for all solutions of linear macromolecular substances[26]. There are various methods for determining molecular weights from osmotic measurements. It was Ostwald's idea[27] to determine the limiting p/c values at zero concentration by graphical extrapolation, and to use this as a basis for calculating the molecular weights.

This method gives satisfactory results with products the molecular weights of which are not too high. Such cases are evident when, in osmotic measurements of the same substance in different solvents, the limiting p/c values at zero concentration are the same, although the increase in the p/c value with increase in concentration in any particular solvent differs because of the differing states of solvation of the fibre molecules[28]. With a product having a very high molecular weight, graphical extrapolation is unreliable.

The molecular weight, especially of eucolloidal substances, can be calculated

TABLE II

TRANSFORMATION OF HOMOLOGOUS POLYMERIC POLYPRENES INTO THE CORRESPONDING POLYMERIC POLYPRANES[20]

Product	$\frac{\eta_{sp}}{c}$	Degree of polymerization (viscometric) $K_m = 1.4 \times 10^{-4}$	Hydrogenated product	$\frac{\eta_{sp}}{c}$	Degree of polymerization (viscometric) $K_m = 1.4 \times 10^{-4}$
Balata (degraded)[21]	0.0371	Unknown[23]	Hydrobalata (degraded)	0.0319	Unknown[23]
Balata[22]	0.154	1,100	Hydrobalata 70% hydrogenated	0.124	900
Balata[21]	0.220	1,600	Hydrobalata 100% hydrogenated	0.219	1,600
Gutta-percha[23]	0.150	1,100	Hydrogutta-percha 89% hydrogenated	0.130	950
Rubber[22]	0.125	900	Hydrorubber 58% hydrogenated	0.134	950
Rubber Fr. I[21]	0.347	2,500	Hydrorubber Fr. I		
			Almost 50% hydrogenated	0.335	2,400
			Almost 100% hydrogenated	0.365	2,600
Rubber Fr. II[21]	0.448	3,200	Hydrorubber Fr. II		
			Almost 50% hydrogenated	0.439	3,100
			Almost 100% hydrogenated	0.422	3,000
Rubber Fr. III[21]	0.480	3,400	Hydrorubber Fr. III		
			Almost 100% hydrogenated	0.412	2,900

more precisely by the formula deduced by Schulz[29], from osmotic pressures at high concentrations:

$$M = \frac{RTc}{p(1-cs)} \tag{2a}$$

where the s values are determined from a curve which is represented by the following equation:

$$s = \frac{1}{c} - \frac{RT}{pM} \tag{2b}$$

The s value is designated by Schulz[30] as the specific active volume. In calculating s values from osmotic measurements, the procedure is to determine in an approximate way the average molecular weight by graphical extrapolation, *i.e.*, according to the first method described, and then to increase or decrease this to a point where all the s values for different osmotic pressures fall on a straight line when a logarithmic scale is used. This straight line can then be used to calculate the average molecular weight from the osmotic measurements. It is interesting in this connection that the s values of rubbers which have been treated in different ways do not fall on the same straight line. When the s values are calculated from the osmotic measurements of Caspari[31], the values of rubbers which have not been degraded lie on a different straight line from those of degraded rubbers. This would lead one to conclude that the macromolecules of these different kinds of rubber are not of the same form—a problem which will be taken up again in a later part of this paper (see Figure 1).

By way of illustration, the calculation of a few molecular weights on the basis of measurements by Caspari are reproduced in Table III.

TABLE III

OSMOTIC MEASUREMENTS OF CASPARI OF RUBBER HYDROCARBONS AT 25° C IN BENZENE

Product	Concentration c (g. per l.)	$p \times 10^3$	$(p/c) \times 10^3$	Specific active volume (s)	Average molecular weight	Average degree of polymerization
Fresh rubber	10.1	3.6	0.36	0.047	131,000	
	14.8	6.6	0.45	0.039	130,000	
	21.0	11.7	0.56	0.031	127,000	
	29.2	21.4	0.73	0.025	129,000	
	35.9	30.7	0.85	0.021	122,000	
	52.6	59.2	1.12	0.016	126,000	
					128,000	1,900
Partially deviscified rubber	10.4	3.6	0.36	0.017	85,000	
	21.7	8.8	0.41	0.014	85,000	
	27.0	11.6	0.43	0.012	85,000	
	33.7	15.8	0.47	0.012	87,000	
	44.5	23.5	0.53	0.010	83,000	
					85,000	1,250
Highly deviscified rubber	20.6	6.0	0.29	0.0084	102,000	
	41.1	14.1	0.34	0.0072	102,000	
	68.9	28.2	0.41	0.0060	102,000	
	99.5	48.4	0.49	0.0050	100,000	
					102,000	1,500

Meyer and Mark[32], and also Kroepelin and Brumshagen[33], made use of the van der Waals equation of perfect gases for calculating molecular weights, on the assumption that the van der Waals constant b is the solvated unit volume of 1 gram of the osmotically active substance. The agreement between the molecular weights calculated by this equation and the values determined by the first method is not very good. That this method is not practical is evident from the fact that the molecular weights of the same crepe rubber are not the same in benezene and in chlorobenzene (see Products No. 3 and 4 in Table IV). On the contrary, the molecular weights calculated from the s values are approximately the same.

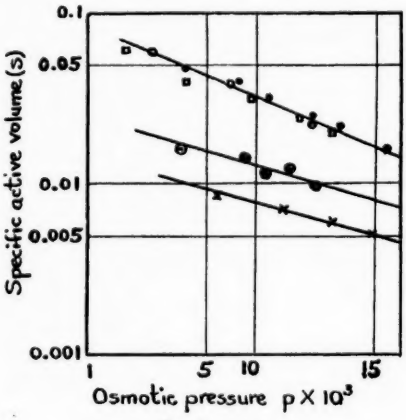


FIG. 1.

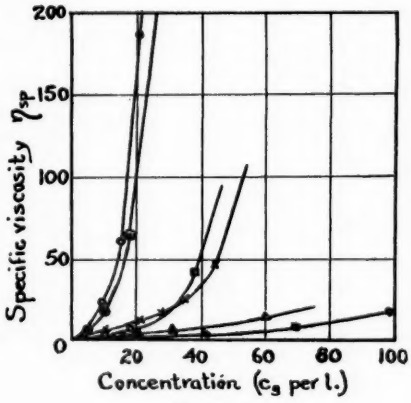


FIG. 2.

FIG. 1.—Relation between specific active volume (s) and osmotic pressue (p) of rubber hydrocarbons derived from the measurements of Caspari.

- ● Fresh rubber in benzene.
- ⊙ Partially deviscified rubber in benzene.
- × Highly deviscified rubber in benzene.
- □ Fresh rubber in light petroleum.
- ○ Partially deviscified rubber in light petroleum.

FIG. 2.—Relation between specific viscosity (η_{sp}) and concentration derived from the viscosity measurements of Caspari.

- ○ Fresh rubber in benzene.
- □ Partially deviscified rubber in benzene.
- ● Highly deviscified rubber.
- ⊙ Fresh rubber in light petroleum.
- × Partially deviscified rubber in light petroleum.
- Δ Gutta-percha in benzene.

Another series of molecular weight determinations was carried out with an ultracentrifuge. The values obtained by this method agree, in their general order of magnitude, with those obtained by the osmotic method[34].

DETERMINATION OF THE $K_{equiv.}$ CONSTANTS OF LOW-MOLECULAR HYDROCARBONS

Before the relations between the η_{sp}/c values and chain lengths of eucolloidal polyprenes and polypranes were studied, viscosity measurements were carried out with solutions of homogeneous, low-molecular, homopolar hydrocarbons in homopolar solvents[35], *i.e.*, solutions of homogeneous polyprenes[36] with known numbers of chain members.

With these products, the $K_{equiv.}$ constants were calculated by Equation (1c)

TABLE IV

AVERAGE DEGREE OF POLYMERIZATION OF RUBBER HYDROCARBONS BASED ON THE LIMITING VALUES AND ON THE s VALUES (MEYER AND MARK, KROEPELIN AND BRUMSHAGEN, CASPARI)

No.	Product	Investigators	Solvent	Limiting p/c at zero concn.	Degree of polymerization from lim (p/c)	Degree of polymerization from s values	Degree of polymerization calculated by the authors
1	Crepe rubber treated with alkali	Meyer and Mark	Benzene	0.11	3,100	3,400	2,200
2	Crepe rubber treated with alkali	Meyer and Mark	Chlorobenzene	0.10	3,400	3,700	2,400
3	Crepe rubber untreated	Meyer and Mark	Benzene	0.05	—	6,300	5,300
4	Crepe rubber untreated	Meyer and Mark	Chlorobenzene	0.05	—	6,200	approx. 2,900
5	Ether-soluble rubber measured at 11° C.	Kroepelin and Brumshagen	Benzene	0.07	4,900	4,400	approx. 3,300
6	Ether-soluble rubber measured at 40° C.	Kroepelin and Brumshagen	Benzene	0.06	6,300	5,500	2,800
7	Fresh rubber	Caspari	Benzene	0.17	2,100	1,900	—
8	Partially deviscified rubber	Caspari	Benzene	0.30	1,200	1,250	—
9	Highly deviscified rubber	Caspari	Benzene	0.24	1,500	1,500	—
10	Fresh rubber	Caspari	Naphtha	0.23	1,550	1,650	—
11	Partially deviscified rubber	Caspari	Naphtha	0.12	3,000	2,900	—
12	Highly deviscified gutta-percha	Caspari	Benzene	0.63	550	—	—

TABLE V

MOLECULAR WEIGHT DETERMINATIONS OF RUBBER WITH AN ULTRACENTRIFUGE

Product	Investigators	Solvent	Molecular weight	Degree of polymerization
Ether-soluble rubber A	Kraemer and Lansing	Ether	400,000	5,900
Ether-soluble rubber B	Kraemer and Lansing	Ether	435,000	6,400
Degraded rubber	Kraemer and Nichols	Ether	69,000	1,000
		Chloroform	63,000	950

to be 1.0×10^{-4} (see Table VI). In the case of paraffins and paraffin derivatives, this constant was 0.95×10^{-4}, which is the value obtained for squalene and hydrosqualene[37]. This value forms the basis of calculations of the number of chain members of rubber hydrocarbons.

TABLE VI

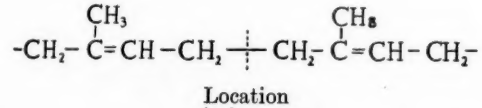
DETERMINATION OF THE $K_{equiv.}$ CONSTANTS OF LOW-MOLECULAR METHYLATED HYDROCARBONS[36]

Product	M	Number of chain members	η_{sp}/c	$K_{equiv.} \times 10^4$
2,6,11,15-Tetramethylhexadecane	282	16	0.00160	1.0
Squalene	410	24	0.00226	0.94
Hydrosqualene	422	24	0.00221	0.92
Dibixan	647	38	0.00396	1.04
Tetrabixan	970	56	0.00566	1.01

To determine the K_m constants and the $K_{equiv.}$ constants of polyprenes and of polypranes, the procedure was formerly to estimate the molecular weights of hemicolloidal members from cryoscopic measurements in benzene, and to calculate the K_m constants and $K_{equiv.}$ constants from viscosity measurements[38]. These values were found to be approximately the same for polypranes and polyprenes[126] (see Table VII).

Calculations of the numbers of chain members from the η_{sp}/c values in column 5 of Table VII, with the $K_{equiv.}$ constant 0.95×10^{-4}, and from these the average degrees of polymerization of the hemicolloidal products, show these latter values to be approximately 25 per cent too small, as is evident by a comparison of columns 8 and 3 in Table VII.

The hemicolloidal polyprenes in Table VII were obtained by thermal degradation of rubber and gutta-percha, carried out by heating in solution, with exclusion of air. In following this procedure, it had formerly been assumed that the original hydrocarbons were composed of long, unbranched fibre molecules, in which case thermal degradation and cracking of these molecules depended wholly on the senitive carbon atoms in the allyl groups, as shown in the following scheme[127]:



Location of cleavage

(The manner in which the end valences are saturated is still unknown)

But in the light of more recent experiments, it seems probable that macromolecules of rubber are not unbranched fibre molecules, but actually are branched.

TABLE VII

DETERMINATION OF THE K_m and $K_{equiv.}$ CONSTANTS OF HEMICOLLOIDAL POLYPRENES AND POLYPRANES BY VISCOSITY AND CRYOSCOPIC MEASUREMENTS IN BENZENE

Product	Molecular weight	Average degree of polymerization	No. of chain members	η_{sp}/c	$K_m \times 10^4$	$K_{equiv.} \times 10^4$	Degree of polymerization calculated from $K_{equiv.} = 0.95 \times 10^{-4}$
Rubber degraded in tetralin	3,400	50	200	0.0154	3.1	0.77	40
Rubber degraded in xylene	4,250	60	250	0.0168	2.7	0.67	45
Gutta-percha degraded in xylene	2,700	40	160	0.0117	3.0	0.73	30
Gutta-percha degraded in tetralin	6,400	95	380	0.0299	3.0	0.80	80
Balata degraded in xylene	7,500	110	440	0.0368 *	3.3	0.84	95
Hydrogutta-percha	5,360	80	310	0.0234	3.0	0.76	60
Hydrorubber III	4,550	65	260	0.0172	2.6	0.66	45
Hydrorubber II	2,770	40	150	0.0131	3.4	0.87	35
Hydrorubber I	1,600	23	90	0.0069	3.0	0.76	18

* Measured in tetralin.

Cracking of these molecules gives rise to much shorter unbranched fragments and, therefore, the K_m values of these hemicolloidal products are much higher ($K_m = 3.0 \times 10^{-4}$) than those of rubber and gutta-percha, whose K_m values lie between 0.8 and 1.7 (see Table XXXVII). On the contrary, the $K_{equiv.}$ values of hemicolloidal polyprenes and polypranes are 25 per cent lower than those of low-molecular, homogeneous polyprenes and polypranes (1.0×10^{-4}), but this is explainable by the fact that these degraded products contain not only simply fibre molecules but also fragments with branched sections. Furthermore it is not impossible that a secondary cyclization takes place during thermal degradation. According to titrations with bromine and iodine, those polyprenes which are formed in tetralin solution at elevated temperatures do not contain the calculated number of double bonds, because a small part of such bonds are lost by cyclization[39].

CALCULATIONS OF THE K_m VALUES AND $K_{equiv.}$ VALUES ON THE BASIS OF EARLIER MEASUREMENTS

In the work of Caspari[40], homologous polymeric rubbers were characterized not only by osmotic measurements, but also by viscometric measurements. These latter measurements were carried out only within the range of gel solutions of various concentrations, and hence not on sol solutions, so it is not possible to calculate directly the η_{sp}/c values which are necessary for calculating, in turn, the K_m and $K_{equiv.}$ constants.

The following relation[41] between the η_{sp}/c_{gm} values of relatively high concentrations and the limiting η_{sp}/c_{gm} values holds true when c_{gm} approaches zero:

$$\log \frac{\eta_{sp}}{c_{gm}} = \lim \left[\log \frac{\eta_{sp}}{c_{gm}} \right] + c_{gm} K_{st} \qquad (3)$$

The applicability of this equation has been demonstrated in viscosity measurements of polystyrene[41], nitrocellulose[42], and rubber solutions[43].

By a corresponding conversion of the viscosity measurements of Caspari, the η_{sp}/c_{gm} values for various concentrations in c_{gm}[44] given in Table VIII are obtained.

An examination of the graphs in Figure 2 make evident that the higher the molecular weight, the greater is the increase in specific viscosity with increase in concentration. This is in accord with the fact that these rubber solutions behave like all other macromolecular compounds with fibre molecules.

When the c_{gm} values are plotted against the log η_{sp}/c_{gm} values as shown in Figure 3, almost straight lines are obtained, from which the limiting values of log η_{sp}/c_{gm} as c_{gm} approaches zero can be read.

The η_{sp}/c_{gm} values, calculated from these $\lim_{c_{gm} \to 0} \left[\frac{\eta_{sp}}{c_{gm}} \right]$ values, are given in column 5 of Table VIII. When the K_m values and $K_{equiv.}$ values are calculated from these η_{sp}/c_{gm} values and from the average degrees of polymerization obtained from osmotic measurements, the values given in column 5 and 6 of Table IX are obtained. These K_m values differ greatly, and only in the case of untreated crude rubber (in benzene) was a K_m value obtained which agreed approximately with the K_m values of hemicolloidal polyprenes and polypranes (see Table VII, column 6), whereas the K_m values of degraded rubbers were far lower.

Since crude rubber gave approximately the correct value, a value of 3×10^{-4} for the K_m constant was used in previous investigations in calculating the

TABLE VIII

Product	Solvent	Concentration c (g. per l.)	c_{gm}	η_r	$\frac{\eta_{sp}}{c_{gm}}$	$\lim_{c_{gm}\to 0} \frac{\eta_{sp}}{c_{gm}}$ from $\lim_{c_{gm}\to 0} \left(\log \frac{\eta_{sp}}{c_n}\right)$
Fresh rubber	Benzene	10.1	0.149	22	141	38
		14.8	0.218	58	261	
		21.0	0.310	188	604	
Partially deviscified rubber	Benzene	10.4	0.153	5.06	26.6	
		21.7	0.319	12.5	36.0	20
		27.0	0.397	16.7	39.5	
		33.7	0.495	23.7	45.9	
		44.5	0.655	45.3	67.7	
Highly deviscified rubber	Benzene	20.6	0.303	2.06	3.50	
		41.1	0.604	4.00	4.96	2.3
		68.9	1.010	8.8	7.7	
		99.5	0.460	16.9	10.9	
Fresh rubber	Light petroleum	5.0	0.073	6.4	74	
		9.9	0.145	17.8	116	
		17.9	0.264	60.0	223	26
		26.7	0.394	710.0	1800	
Partially deviscified rubber	Light petroleum	9.1	0.134	3.75	20.5	14
		17.6	0.259	8.6	29.0	
		36.3	0.533	35.0	64.0	
Highly deviscified gutta-percha	Benzene	12.6	0.185	2.10	5.93	
		20.4	0.300	2.64	5.47	3.8
		30.4	0.447	4.77	8.45	
		60.3	0.887	15.9	16.8	

TABLE IX

CALCULATION OF THE K_m AND $K_{equiv.}$ CONSTANTS FROM MEASUREMENTS BY CASPARI

Product	Solvent	Average degree of polymerization	No. of chain members	$\frac{\eta_{sp}}{c}$	$Km \times 10^4$	$K_{equiv.} \times 10^4$
Fresh rubber	Benzene	1,900	7,600	0.56	3.0	0.74
Partially deviscified rubber	Benzene	1,250	5,000	0.29	2.3	0.58
Highly deviscified rubber	Benzene	1,500	6,000	0.034	0.23	0.057
Fresh rubber	Light petroleum	1,650	6,600	0.38	2.3	0.57
Partially deviscified rubber	Light petroleum	2,900	11,600	0.206	0.7	0.18
Gutta-percha	Benzene	550	2,200	0.056	1.0	0.25

molecular weights of rubber and balata from viscosity measurements. It is surprising that a degraded rubber has a higher molecular weight than untreated crude rubber (see Table IX). It is possible that the effects of light and air are not always confined to autoöxidative degradation, but that also a uniting of the fibre molecules[45] by oxygen bridges may take place. In this way, branched molecules of very irregular shape are formed. In favor of this hypothesis are also the small K_m and $K_{equiv.}$ values of partially deviscified rubber (in benzene and in light petroleum) shown in Table IX.

In earlier work[46], the K_m and $K_{equiv.}$ values of balata and hydrorubber were determined, and it was found that the values of balata were approximately the same as those of hemicolloidal polyprenes and polypranes (compare Table X with Table VII). On the contrary, the $K_{equiv.}$ value of a hydrorubber was much lower than the $K_{equiv.}$ values of hemicolloidal rubbers.

TABLE X

CALCULATION OF THE K_m AND $K_{equiv.}$ CONSTANTS FROM MEASUREMENTS OF G. V. SCHULZ

Product	Solvent	Average degree of polymerization	No. of chain members	$\frac{\eta_{sp}}{c}$	$K_m \times 10^4$	$K_{equiv.} \times 10^4$
Balata	Toluene	650	2,600	0.180	2.8	0.70
Hydrorubber	Toluene	1,050	4,200	0.181	1.7	0.43

Kraemer and Lansing[46] determined the molecular weights of two types of rubber by the ultracentrifuge method and, in addition to this, characterized the rubbers by measuring their viscosities in ether solutions. From these viscosity data, the η_{sp}/c values were calculated[47]. The $K_{equiv.}$ values obtained from these measurements were approximately 10 times smaller than those of hemicolloidal products[48].

TABLE XI

CALCULATION OF THE K_m AND $K_{equiv.}$ VALUES FROM THE MEASUREMENTS OF KRAEMER AND LANSING

Product	Average degree of polymerization	No. of chain members	η_{sp}/c	$K_m \times 10^4$	$K_{equiv.} \times 10^4$
Ether-soluble rubber A	5,900	23,600	0.183	0.31	0.08
Ether-soluble rubber B	6,400	25,600	0.202	0.32	0.08

It is evident, therefore, that none of the earlier experiments give any clue to the magnitudes of the K_m and $K_{equiv.}$ constants of rubber hydrocarbons and, furthermore, they do not make it possible to decide whether the viscosity law of fibre molecules holds true of solutions of these hydrocarbons. Consequently it has been impossible up to the present time to settle the question whether the macromolecules of these hydrocarbons are long, unbranched fibre molecules in solutions. In view of this, the K_m and $K_{equiv.}$ values of a series of rubber hydrocarbons were determined anew, and the results are described in the following pages.

Difficulties were immediately encountered in this new investigation. First of all, both in the solid state and in solution, crude polyprenes (rubber, gutta-percha, balata) are relatively insensitive to oxygen because of the antioxidants which they

contain[49]. On the contrary, after removal of these antioxidants, these hydrocarbons are so extraordinarily unstable that it is difficult to work with them. This raises the question whether it would not be advisable to work with the crude products without any preliminary purification. Since, however, it is not known in what way the antioxidants influence the viscosity of the solutions, and to what extent they affect the osmotic measurements, only carefully purified products were used in the work to be described. This seemed advisable in spite of the fact that it added great difficulties to the work.

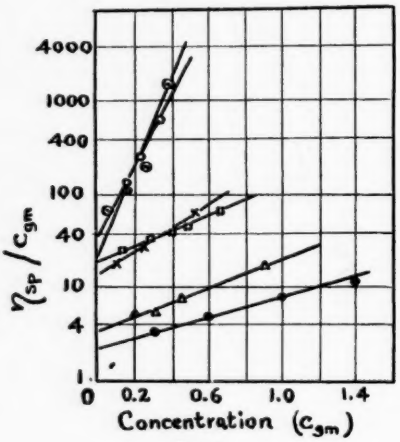


FIG. 3.

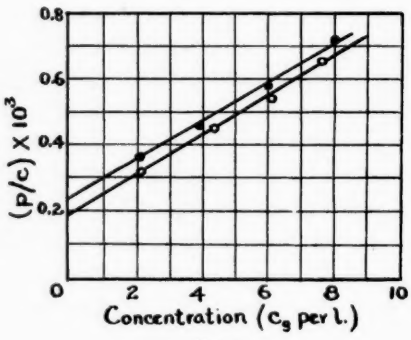


FIG. 4.

FIG. 3.—Graphical determination of the limiting $(\eta_{sp})/c_{gm}$ value as c_{gm} approaches zero, derived from viscosity measurements of Caspari.

○ Fresh rubber in benzene.
□ Partially deviscified rubber in benzene.
● Highly deviscified rubber in benzene.
⊙ Fresh rubber in light petroleum.
△ Gutta-percha in benzene.
× Partially deviscified rubber in light petroleum.

FIG. 4.—(p/c)-c Curves of gutta-percha in carbon tetrachloride at 27° C.

○ Gutta-percha I.
● Gutta-percha II.

DETERMINATION OF THE K_m AND $K_{equiv.}$ VALUES OF BALATA AND GUTTA-PERCHA

PREPARATION OF THE STARTING MATERIALS

Gutta-percha and balata were used for determining the K_m and $K_{equiv.}$ values, because, judged by roentgenographic investigations, these hydrocarbons crystallize well[50], and are, in fact, identical[51]. It was assumed that, like all substances which are composed of fibre molecules, their form is not altered in any fundamental way by solution. This meant, therefore, that macromolecules of these hydrocarbons exist in solution in the form of long, unbranched fibre molecules.

The gutta-percha and balata were prepared from latex[52], and it was hoped therefore that the macromolecules of these hydrocarbons would contain no secondary branchings as a result of autoöxidation, as happens in the case of commercial gutta-percha and balata[53].

To obtain the hydrocarbons, they were precipitated from the latices by a

mixture of acetone and methanol[54]. The crude products were extracted with acetone for 12 hours to remove resins, and solutions in carbon tetrachloride of approximately 1 per cent concentration at 40° C were prepared from the acetone-insoluble residues. These highly viscous solutions were turbid, but this turbidity was removed by centrifuging with animal charcoal. This process was repeated until absolutely clear solutions were obtained by filtration through a Soxhlet filter. From these clear solutions, the hydrocarbons were precipitated by adding double the quantity of a mixture of 1 part of methanol and 2 parts of acetone at room temperature. When the solutions were allowed to flow into the mixture of acetone and methanol, while stirring, the products were obtained in a fibrous form. These were removed by filtration, were washed with acetone, and were dried in a high vacuum.

Purification of the hydrocarbons as described above must be carried out in the absence of oxygen; actually the procedure was carried out in carefully purified nitrogen and in air-free carbon dioxide. In addition to this precaution, brown-glass apparatus or clear-glass apparatus painted with red lamp lacquer was used, so that light was excluded. Only in this way was it possible to avoid any change in the extremely sensitive polyprenes as a result of autoöxidation or of the effects of light. According to the analyses shown in Table XII, the hydrocarbons obtained by the procedure described were of satisfactory purity[55], in fact they contained less than 0.03 per cent of nitrogen.

TABLE XII

ANALYSIS OF GUTTA-PERCHA AND BALATA HYDROCARBONS[56]

Substance	Average degree of polymerization	Carbon (percentage)	Hydrogen (percentage)	Nitrogen (percentage)	Ash
Gutta-percha I	1,900	88.45	11.64	0.03	Ash-free
Gutta-percha II	1,550	88.20	11.77	0.03	Ash-free
Balata I	1,300	88.15	11.78	0.03	Ash-free
Calculated for $(C_5H_8N)_x$		88.16	11.84	—	—

OSMOTIC DETERMINATIONS OF THE MOLECULAR WEIGHTS OF BALATA AND GUTTA-PERCHA

The molecular weight determinations were carried out in carbon tetrachloride and in toluene, in the type of osmometer described by Schulz[57]. Because of the sensitivity of these solutions, the measurements had to be made with rigorous exclusion of air and light. It was found that when a chromium-plated brass osmometer was employed, degradation of the hydrocarbons took place, particularly in carbon tetrachloride. This phenomenon was evident by the fact that the osmotic pressure was not constant, but increased steadily, while the viscosity of the solutions decreased. For the work at hand, an osmometer of V-4-A steel[58] was found to be satisfactory.

To find out whether or not the dissolved hydrocarbons changed during the measurements, the specific viscosities of the solutions were determined before and after the measurements. In evaluating the viscosity data, osmotic measurements were carried out only when the specific viscosity of a solution was at the most 5 per cent less at the end of an experiment than it was at the beginning. Osmotic measurements in carbon tetrachloride were less accurate than those in toluene for, in the latter solvent, the hydrocarbons changed slightly, even when an osmometer made of V-4-A steel was used.

To calculate molecular weights from osmotic pressures at different concentra-

TABLE XIII

OSMOTIC MEASUREMENTS OF GUTTA-PERCHA AND BALATA HYDROCARBONS IN TOLUENE AT 27° C

Substance	Solvent	Concentration c (g. per l.)	Osmotic pressure ($p \times 10^3$)	$(p/c) \times 10^3$	Specific active volume (s)	Average molecular weight	Average degree of polymerization
Gutta-percha I	Carbon tetrachloride	2.19	0.71	0.32	0.18	125,000	
		4.43	1.98	0.45	0.13	129,000	
		6.07	3.28	0.54	0.105	126,000	
		7.74	5.06	0.66	0.091	128,000	
						127,000	1,900
Gutta-percha II	Carbon tetrachloride	2.04	0.73	0.36	0.18	109,000	
		3.96	1.80	0.45	0.13	111,000	
		5.96	3.33	0.56	0.105	115,000	
		8.00	5.68	0.71	0.087	115,000	
						112,000	1,650
Gutta-percha III	Toluene	1.03	0.29	0.28	0.160	104,000	
		2.02	0.64	0.32	0.124	104,000	
		3.07	1.05	0.34	0.105	105,000	
		4.04	1.54	0.38	0.096	106,000	
		6.00	2.63	0.44	0.078	106,000	
		8.07	4.20	0.52	0.069	104,000	
						105,000	1,550
Balata I	Toluene	1.04	0.35	0.33	0.155	88,000	
		2.05	0.75	0.36	0.113	88,000	
		3.01	1.19	0.39	0.098	88,000	
		4.01	1.78	0.44	0.092	88,000	
		5.01	2.42	0.48	0.083	87,000	
		6.01	3.07	0.51	0.075	87,000	
						88,000	1,300
Balata II	Toluene	2.17	0.72	0.33	0.120	97,000	
		4.10	1.78	0.43	0.090	90,000	
		6.03	2.79	0.46	0.078	101,000	
		8.30	4.51	0.54	0.068	104,000	
						99,000	1,450

tions, the limiting p/c values with approach of c to zero were derived. The molecular weights were derived also from Equation (2a) of Schulz. The relation between the specific active volume s and the osmotic pressure p is shown graphically in Figure 6.

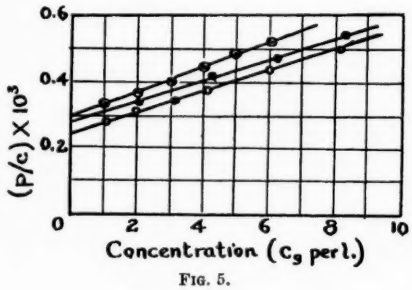


FIG. 5.

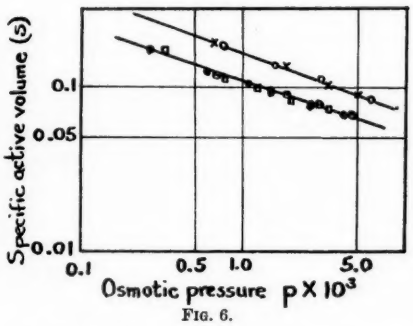


FIG. 6.

FIG. 5.—(p/c)-c Curves of gutta-percha and balata in toluene at 27° C.

○ Gutta-percha II.
⊙ Balata I.
● Balata II.

FIG. 6.—Relation of specific active volume (s) and osmotic pressure (p) of gutta-percha and balata.

× Gutta-percha I in carbon tetrachloride.
○ Gutta-percha II in carbon tetrachloride.
● Gutta-percha II in toluene.
□ Balata I in toluene.
⊙ Balata II in toluene.

Following this procedure, the molecular weights shown in Table XII were obtained.

The molecular weights obtained by the method of limits are approximately the same as those calculated from the specific activity-volume (s) values, as is evident in Table XIV. This tabulated summary shows to what extent the molecular weights obtained by the method of limits would have to change so that the s values would fall on a straight line.

TABLE XIV

AVERAGE DEGREES OF POLYMERIZATION OF GUTTA-PERCHA AND BALATA HYDROCARBONS ACCORDING TO THE METHOD OF LIMITS AND ACCORDING TO THE SPECIFIC ACTIVITY-VOLUME (s) VALUES

Substance	Solvent	$\lim_{c\to 0}(p/c)$	Average degree of polymerization from $\lim_{c\to 0}(p/c)$	Average degree of polymerization from the s values
Gutta-percha I	Carbon tetrachloride	0.19	1,900	1,900
Gutta-percha II	Carbon tetrachloride	0.24	1,500	1,650
Gutta-percha II	Toluene	0.24	1,500	1,550
Balata I	Toluene	0.29	1,200	1,300
Balata II	Toluene	0.28	1,300	1,450

DETERMINATION OF THE K_m AND $K_{equiv.}$ VALUES

The viscosity measurements were carried out at 20° C, with rigorous exclusion of air and light, through the range of sol solutions, the specific viscosities of which

TABLE XV

VISCOSITY MEASUREMENTS IN TOLUENE AND IN CARBON TETRACHLORIDE AT 20° C

Substance	Solvent	Concentration c (g. per l.)	η_r	η_{sp}/c	$\frac{\eta_{sp}/c \text{ in toluene}}{\eta_{sp}/c \text{ in tetrachloride}}$
Gutta-percha I	Carbon tetrachloride	0.504	1.154	0.305	—
		0.496	1.151	0.305	
Gutta-percha II	Toluene	0.400	1.084	0.210	
		0.400	1.084	0.210	0.79
Gutta-percha II	Carbon tetrachloride	0.508	1.133	0.262	
		0.552	1.147	0.267	—
Balata I	Toluene	0.407	1.067	0.165	
		0.424	1.070	0.165	0.85
Balata I	Carbon tetrachloride	0.460	1.089	0.193	—
		0.460	1.089	0.193	
Balata II	Toluene	0.468	1.089	0.190	
		0.460	1.085	0.185	—

were below 0.20. To exclude light, all apparatus, including the viscometer and flask, was made of dark brown glass. By using an overflow viscometer, the operations could be carried out quite conveniently in the absence of air. It was found that, in this apparatus, the specific viscosities of solutions remained constant even after standing for days. Several viscosity measurements were carried out with every sample and, under proper conditions, the η_{sp}/c values differed only 5 per cent at the most.

To be sure of the accuracy of these difficult measurements, the results of two measurements are, in most cases, given in the following pages[59]. The η_{sp}/c values, were somewhat higher in carbon tetrachloride than in toluene, because the former solvent has a greater solvating action than the latter on the hydrocarbons[60]. This is, in fact, true of all hydrocarbons[61]. The ratio of the η_{sp}/c values in the two solvents is practically constant.

Further viscosity measurements were made at 20° C and at 60° C. The dependence on temperature, *i.e.*, the ratio of the viscosity at 60° C to that at 20° C, was approximately 0.9, which is approximately the same as that of low-molecular hydrocarbons in benzene[62].

TABLE XVI

TEMPERATURE RELATIONSHIP OF THE η_{sp}/c VALUES AT 20° C AND AT 60° C

Substance	Solvent	η_{sp}/c at 20° C	η_{sp}/c at 60° C	$\frac{\eta_{sp}/c \text{ at } 60° \text{ C}}{\eta_{sp}/c \text{ at } 20° \text{ C}}$
Gutta-percha II	Toluene	0.210	0.190	0.90
		0.210	0.190	0.90
Balata I	Toluene	0.165	0.147	0.89
		0.165	0.146	0.89
Balata II	Toluene	0.190	0.177	0.93
		0.185	0.176	0.95

The K_m and $K_{equiv.}$ values were obtained from the average degrees of polymerization, which were derived from osmotic measurements (see Table XIII), and from the viscosity numbers (see Table XVI). They show deviations of 10 per cent, and are approximately one-half as great as the calculated values of hemicolloidal polyprenes and polypranes, and are one-third as great as those of pure low-molecular hydrocarbons of the isoprene series. Accordingly it is not possible to calculate the average molecular weights of gutta-percha and balata from viscosity measurements with the K_m constants found for low-molecular compounds. This will be discussed in more detail at the end of this work.

DETERMINATION OF THE K_m VALUES AND $K_{equiv.}$ VALUES OF RUBBER

PREPARATION OF RUBBER HYDROCARBONS

As described in the preceding section, the K_m values of balata and gutta-percha are much lower than the calculated values. They are also lower than the values of hemicolloidal substances, and are lower than the K_m values of raw rubber, accordnig to the measurements of Caspari. In view of this, rubber was studied further to ascertain whether a similarly high K_m value would be obtained, as was calculated from the data of Caspari.

The method of purification described by Pummerer and Pahl[63] was followed to obtain pure rubber. In the measurements themselves, only the relatively low-polymerized ether-soluble portions were used[64] for, according to earlier work[65], the ether-insoluble, benzene-soluble portion of the mixture of polyprenes is of

TABLE XVII

DETERMINATION OF THE K_m AND $K_{equiv.}$ CONSTANTS OF GUTTA-PERCHA AND BALATA HYDROCARBONS

Substance	Solvent	η_{sp}/c at 20° C	Average degree of polymerization from the η values	No. of chain-members (n)	$K_m \times 10^4$	$K_{equiv.} \times 10^4$
Gutta-percha I	Carbon tetrachloride	0.305	1,900	7,600	1.6	0.40
Gutta-percha II	Carbon tetrachloride	0.265	1,650	6,600	1.6	0.40
Gutta-percha II	Toluene	0.210	1,550	6,200	1.4	0.34
Balata I	Toluene	0.165	1,300	5,200	1.3	0.32
Balata II	Toluene	0.188	1,450	5,800	1.3	0.33

TABLE XVIII

ANALYSIS OF RUBBER HYDROCARBONS

Product	Average degree of polymerization	Carbon (percentage)	Hydrogen (percentage)	Nitrogen (percentage)	Ash subtraction (percentage by from the analysis)
Ether-soluble rubber (treated with alkali by the method of Pummerer)	1,600	88.39	11.64	<0.05	0.15
Rubber treated with aluminum oxide	5,100	87.95	11.79	—	0.6 *
Ether-soluble rubber					
Easily soluble fraction	3,600	87.37	11.66	—	0.19
Difficultly soluble fraction	2,700	87.50	11.72	—	0.19
Calculated for $(C_5H_8N)x$	—	88.16	11.84		

* This high ash content is attributable to aluminum oxide in colloidal solution.

such molecular weight that it is unsuitable for osmotic measurements. Furthermore, this type of rubber gave a too low K_m value (see Table XXIII). It seemed possible, therefore, that, through the agency of traces of oxygen, linking of the fibre molecules took place during purification, with resulting formation of products composed of branched macromolecules. Macromolecules with this type of structure would naturally give only small K_m values.

To prepare a rubber which had undergone the least possible change, the long operation involved in its purification was avoided and, instead, an approximately 0.5 per cent solution of rubber (the solution was of crude rubber prepared from latex[67]) was agitated with aluminum oxide to remove proteins[66], the aluminum oxide was removed by centrifuging, the solution was filtered through a cotton filter, and finally the rubber was precipitated by adding acetone. Even after such solution and reprecipitation, the product still contained an appreciable ash.

Since this rubber also gave a too low K_m value (see Table XXIII), ether-soluble rubber was prepared from latex, without treating it further with chemicals, so as to avoid any possible secondary change in the macromolecules. The rubber was precipitated from latex by acetone, this crude rubber was extracted with acetone, and then with ether in the same apparatus. The first fraction which was easily soluble in ether was discarded, and only the second and third fractions were saved for the experiments. In spite, however, of this careful purification, even this rubber did not show the expected K_m values; furthermore, its carbon content was too low.

In the preparation of all these samples of rubber, the same precautionary measures were taken as were employed in the preparation of gutta-percha and balata. Light was excluded by using brown-glass apparatus, and air was rigorously excluded by carrying out the experiments in nitrogen or carbon dioxide. The hydrocarbons obtained in this way were, in all cases, free of nitrogen.

When the purified rubbers were exposed for some time to light and air, they became insoluble[68], as a result of a linking of the fibre molecules into a system of three-dimensional macromolecules. In this way, a soluble polyprene with unlimited swelling capacity is transformed into a insoluble product with limited capacity. This linking is induced by traces of atmospheric oxygen. To prevent the rubbers from being transformed into these insoluble products, the samples were kept in the form of solutions. Toluene was chosen as the solvent, and the concentrations of the solutions were determined by evaporation of measured volumes.

Osmotic Measurements of Rubber Hydrocarbons

Osmotic measurements of solutions of rubber hydrocarbons were made in toluene, since carbon tetrachloride solutions are unstable. In this case too, cells of V-4-A steel were employed for the measurements. In calculating molecular weights from osmotic data, the same procedure was followed as that used in determining the molecular weights of gutta-percha and balata.

When the limiting p/c values were determined by graphic extrapolation, the surprising fact was found that the (p/c)-c curves of two products crossed one another. If the different samples of rubber represented homologous polymers, their curves should have been parallel. The contrary course of the curves indicates that the macromolecules of these different rubbers do not have exactly the same forms. The K_m values, which were determined afterwards, also were found to differ as a result of different branchings of the macromolecules.

TABLE XIX

OSMOTIC MEASUREMENTS OF RUBBER HYDROCARBONS IN TOLUENE AT 27° C

Product	Concentration c (g. per l.)	$p \times 10^3$	$(p/c) \times 10^3$	Specific active volume (s)	Average molecular weight	Average degree of polymerization
Ether-soluble rubber (treated with alkali by the method of Pummerer)	1.95	0.58	0.30	0.105	104,000	
	3.87	1.21	0.31	0.080	114,000	
	5.96	2.10	0.35	0.064	112,000	
					110,000	1,600
Crude rubber (treated with aluminum oxide)	2.76	0.31	0.11	0.140	357,000	
	3.85	0.48	0.13	0.120	369,000	
	5.86	0.94	0.16	0.090	322,000	5,100
Ether-soluble rubber						
Easily soluble fraction	2.20	0.34	0.15	0.155	240,000	
	4.10	0.76	0.19	0.120	260,000	
	6.30	1.65	0.26	0.094	230,000	
	7.50	2.32	0.31	0.082	208,000	
	10.60	3.75	0.35	0.071	285,000	3,600
Difficultly soluble fraction	2.00	0.35	0.17	0.110	182,000	
	3.90	0.74	0.19	0.080	188,000	
	5.90	1.23	0.21	0.064	190,000	
	8.00	2.00	0.25	0.052	170,000	2,700

The limiting p/c values as the concentration approached zero were determined by graphical extrapolation, and from these values the average molecular weights were calculated. The average molecular weights obtained by this method were then used for calculating the s values by the method already described (see page 476).

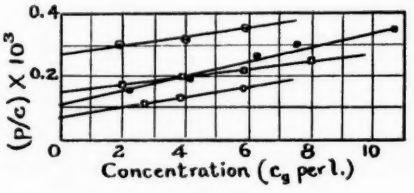


FIG. 7.

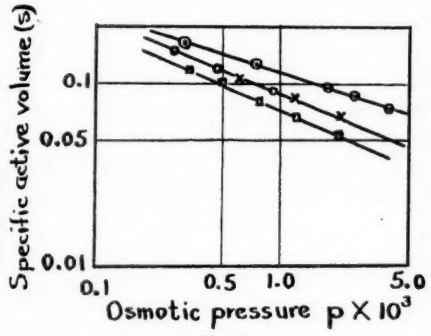


FIG. 8.

FIG. 7.—(p/c)-c Curves of rubber hydrocarbons in toluene at 27° C.

⊙ Rubber treated with alkali by the Pummerer method (ether-soluble)
○ Rubber treated with aluminum oxide.
Ether-soluble rubber:
● Easily soluble fraction.
□ Difficultly soluble fraction.

FIG. 8.—Relation between specific volume (s) and osmotic pressure (p) of rubber hydrocarbons.

× Rubber treated with alkali by the Pummerer method (ether soluble).
○ Rubber treated with aluminum hydroxide.
Ether-soluble rubber:
⊙ Easily soluble fraction.
□ Difficultly soluble fraction.

TABLE XX

AVERAGE DEGREES OF POLYMERIZATION OF RUBBER HYDROCARBONS BY THE METHOD OF LIMITS AND FROM THE s VALUES

Product	$\lim_{c\to 0} (p/c)$	Average degree of polymerization from $\lim_{c\to 0} (p/c)$	Average degree of polymerization from s values
Either-soluble rubber (treated with alkali by the method of Pummerer)	0.27	1,350	1,600
Rubber treated with aluminum oxide	0.07	5,200	5,100
Ether-soluble rubber			
Easily soluble fraction	0.105	3,400	3,600
Difficultly soluble fraction	0.14	2,500	2,700

Whereas the s values of the different samples of ablata and gutta-percha fall on one straight line, this is not the case with rubber, and a different straight line had to be calculated for almost every product. Furthermore, these s-p lines are not in most cases the same as those constructed on a basis of the osmotic measurements of Caspari. These differences lead to the conclusion that the different polyprenes are not strictly homologous polymers, as previously assumed.

Table XX gives a comparison of the molecular weights of rubber hydrocarbons obtained by the method of limits and from the s values (see Table XIV).

Determination of the K_m and $K_{equiv.}$ Values of Rubber Hydrocarbons

Viscosity measurements of solutions of rubber hydrocarbons were carried out in toluene at 20° C, with complete exclusion of air and light.

The dependence of the viscosity on the temperature[69], and therefore the ratios of the η_{sp}/c values at 60° C to those at 20° C, are approximately 0.95, *i.e.*, about the same as those of gutta-percha and balata hydrocarbons.

Table XXI

Viscosity Measurements of Solutions of Rubber Hydrocarbons in Toluene at 20° C

Product	Average degree of polymerization from s values	Concentration c (g. per l.)	η_r	η_{sp}/c
Ether-soluble rubber (treated with alkali by the method of Pummerer)	1,600	0.768	1.097	0.126
		0.744	1.093	0.125
Rubber treated with aluminum oxide	5,100	0.164	1.150	0.915
		0.172	1.152	0.885
Ether-soluble rubber				
Easily soluble fraction	3,600	0.376	1.149	0.397
		0.528	1.201	0.381
Difficultly soluble fraction	2,700	0.448	1.212	0.473
		0.500	1.224	0.448

Table XXII

Comparison of the η_{sp}/c Values of Solutions of Rubber Hydrocarbons at 20° C and at 60° C

Product	Average degree of polymerization from s values	η_{sp}/c at 20° C	η_{sp}/c at 60° C	$\frac{\eta_{sp}/c \text{ at } 60° \text{ C}}{\eta_{sp}/c \text{ at } 20° \text{ C}}$
Ether-soluble rubber (treated with alkali by the method of Pummerer)	1,600	0.126	0.120	0.95
		0.125	0.122	0.97
Rubber treated with aluminum oxide	5,100	0.915	0.820	0.90
		0.885	0.810	0.91
Ether-soluble rubber				
Easily soluble fraction	3,600	0.397	0.373	0.94
		0.381	0.386	0.99
Difficultly soluble fraction	2,700	0.473	0.447	0.95
		0.448	0.434	0.97

From the average degrees of polymerization determined from the osmotic measurements and the viscosity numbers, the K_m and $K_{equiv.}$ values of the rubber hydrocarbons were then determined.

These values are much lower than those of low-molecular homogeneous products (see Table VI). In the present experiments, no such high K_m value as that obtained by calculation from data on crude rubber of Caspari was observed[70]. In contrast to gutta-percha and balata, the K_m values of individual rubber hydrocarbons are not the same. This is evidence that completely polymerically homologous polyprenes are not present, but that the individual products differ in structure.

TABLE XXIII

DETERMINATION OF THE K_m AND $K_{equiv.}$ VALUES OF RUBBER HYDROCARBONS

Product	η_{sp}/c at 20° C	Average degree of polymerization from s values	No. of chain members (n)	$K_m \times 10^4$	$K_{equiv.} \times 10^4$
Ether-soluble rubber (treated wth alkali by the method of Pummerer)	0.126	1,600	6,400	0.8	0.20
Rubber treated with aluminum oxide	0.900	5,100	20,400	1.7	0.44
Ether-soluble rubber					
Easily soluble fraction	0.389	3,600	14,400	1.1	0.27
Difficultly soluble fraction	0.460	2,700	10,800	1.7	0.43

TABLE XXIV

ANALYSIS OF MASTICATED, OXIDIZED AND CYCLIZED RUBBER HYDROCARBONS

Product	Average degree of polymerization	Carbon (percentage)	Hydrogen (percentage)	Oxygen (percentage)	Ash (percentage calculated by subtraction)
Masticated rubber (technical)					
Easily soluble fraction	1,350	85.83	11.86	3.31	Ash-free
Difficultly soluble fraction	2,300	86.34	11.79	1.87	0.33
Masticated rubber					
Easily soluble fraction	1,350	84.63	11.52	3.85	Ash-free
Difficultly soluble fraction	1,100	85.64	11.88	2.48	Ash-free
Crepe rubber I oxidized by potassium permanganate	1,950	87.28	11.97	0.75	Ash-free
Crepe rubber II oxidized by potassium permanganate					
Easily soluble fraction	1,250	88.16	11.90	—	Ash-free
Difficultly soluble fraction	1,850	86.45	11.78	1.75	Ash-free
Cyclorubber prepared with tin tetrachloride	540	86.63	11.26	2.17	Ash-free
Calculated for $(C_5H_8)_x$	—	88.16	11.84	—	—

DETERMINATION OF THE K_m AND $K_{equiv.}$ VALUES OF MASTICATED, OXIDIZED AND CYCLIZED RUBBERS

Preparation of the Products

Two masticated rubbers were studied. The first was a technical product[71]; the second was prepared from crude rubber which had been precipitated from latex by acetone, and masticated for 1 hour at 130° C with access to air. These two samples were purified by extraction with acetone. Product I was dissolved in toluene and fractionally precipitated by acetone. The first precipitate, which contained protein, was discarded, and only the second and third fractions were examined. Product II was extracted with ether after purification with acetone; here again the first extract was discarded.

These masticated rubbers too were extraordinarily sensitive, and were treated further like the other rubbers. They contained 2-3 per cent of oxygen, which was absorbed during mastication.

To study the effect of oxygen on rubber, a solution of rubber in carbon tetrachloride was treated with potassium permanganate in acetone[72]. To this end, a solution of 3 grams of potassium permanganate in 200 cc. of acetone was allowed to run into a solution of 10 grams of crepe rubber in 1.5 liters of carbon tetrachloride at room temperature, with agitation. The color of the potassium permanganate disappeared after standing about one-half hour, and the viscosity of the solution decreased considerably. Before proceding further, the manganese dioxide was filtered off through a cotton filter. By addition of acetone to the still brownish filtrate[73], rubber containing manganese dioxide was precipitated. After the solution was completely clear, further addition of acetone yielded a difficultly soluble fraction and an easily soluble fraction. These fractions were kept in toluene solution under nitrogen, for solid, purified rubbers of this kind become insoluble very rapidly.

Finally a cyclorubber was prepared by the action of tin tetrachloride on rubber[74]. Under these conditions, as proved earlier[75], ring closure takes place in a way strictly analogous to that which takes place in the transformation of aliphatic into cyclic terpenes. To prepare the cyclorubber, 25 grams of tin tetrachloride was added, with vigorous agitation, to a solution of 7 grams of rubber in 1 liter carbon tetrachloride. The viscosity of the solution decreased considerably as result of the reaction and, after agitation for one day, the slightly viscous solution was treated with acetone containing hydrogen chloride. The cyclorubber was repeatedly dissolved in carbon tetrachloride and reprecipitated. In this way, it was possible to obtain an ash-free cyclorubber having an extremely low chlorine content.

Osmotic Measurements of Masticated, Oxidized, and Cyclized Rubbers

When the limiting p/c values were determined by graphical extrapolation, it was found, quite unexpectedly, that the (p/c)-c curves of two products crossed one another. The macromolecules of these differently prepared rubbers therefore have different forms, and they are not strictly homologous polymeric products.

The s values of masticated rubbers, like those of cyclorubbers, fall approximately on the same straight line which is constructed from calculations based on the measurements of Caspari. Surprisingly, this is also true of cyclized rubber, although the K_m value of the latter is very different from that of masticated rubber. On the contrary, rubbers obtained by reaction with potassium permanganate give s-p straight lines which are somewhat more level.

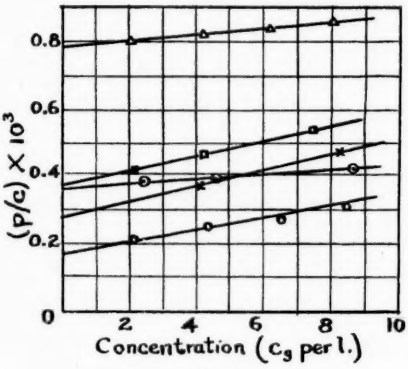


FIG. 9.

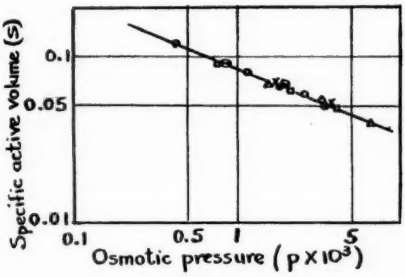


FIG. 10.

FIG. 9.—(p/c)-c Curves of masticated rubber and cyclo-rubber in toluene at 27° C.

Masticated rubber (technical):
× Easily soluble fraction.
○ Difficultly soluble fraction.
Masticated rubber:
⊙ Easily soluble fraction.
□ Difficultly soluble fraction.
Cyclorubber:
Δ Difficultly soluble fraction.

FIG. 10.—Relation between specific active volume (s) and osmotic pressure (p) of masticated rubber and cyclorubber.

Masticated rubber (technical):
× Easily soluble fraction.
○ Difficultly soluble fraction.
Masticated rubber:
⊙ Easily soluble fraction.
□ Difficultly soluble fraction.
Cyclorubber:
Δ Difficultly soluble fraction.

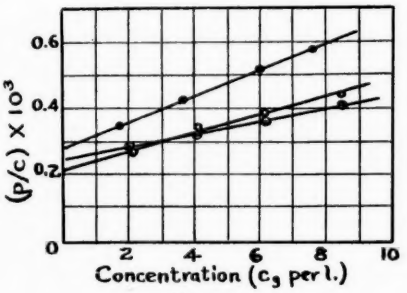


FIG. 11.

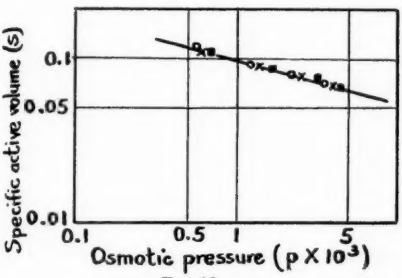


FIG. 12.

FIG. 11.—(p/c)-c Curves of rubber oxidized by potassium permanganate, in toluene at 27° C.

○ Rubber I oxidized by potassium permanganate.
Rubber II oxidized by potassium permanganate.
⊙ Easily soluble fraction.
● Difficultly soluble fraction.

FIG. 12.—Relation between specific volume (s) and osmotic pressure (p) of rubbers oxidized by potassium permanganate.

○ Rubber I oxidized by potassium permanganate.
Rubber II oxidized by potassium permanganate.
■ Easily soluble fraction.
× Difficultly soluble fraction.

TABLE XXV

OSMOTIC MEASUREMENTS OF MASTICATED, OXIDIZED AND CYCLIZED RUBBERS IN TOLUENE AT 27° C

Product	Concentration c (g. per l.)	$p \times 10^3$	$(p/c) \times 10^3$	Specific active volume (s)	Average molecular weight	Average degree of polymerization
Masticated rubber (technical)						
Easily soluble fraction	4.15	1.58	0.38	0.070	91,000	
	8.23	3.76	0.46	0.051	93,000	
					92,000	1,350
Difficultly soluble fraction	2.08	0.44	0.21	0.121	155,000	
	4.32	1.10	0.25	0.080	147,000	
	6.45	1.78	0.27	0.070	167,000	
	8.24	2.58	0.31	0.058	151,000	
					155,000	2,300
Masticated rubber						
Easily soluble fraction	2.4	0.89	0.37	0.095	86,000	
	4.6	1.80	0.39	0.068	91,000	
	8.7	3.70	0.42	0.047	97,000	
					92,000	1,350
Difficultly soluble fraction	2.1	0.86	0.41	0.092	74,000	
	4.2	1.91	0.46	0.066	75,000	
	7.4	4.00	0.54	0.049	72,000	
					74,000	1,100
Crepe rubber I oxidized by potassium permanganate	2.1	0.58	0.28	0.115	120,000	
	4.1	1.30	0.32	0.091	120,000	
	6.2	2.23	0.36	0.080	133,000	
	8.5	3.52	0.41	0.070	148,000	
					133,000	1,950
Crepe rubber II oxidized by potassium permanganate						
Easily soluble fraction	1.8	0.63	0.35	0.110	87,000	
	3.8	1.65	0.43	0.086	84,000	
	6.0	3.05	0.51	0.074	87,000	
	7.5	4.15	0.56	0.068	91,000	
					87,000	1,250
Difficultly soluble fraction	2.2	0.59	0.27	0.107	121,000	
	4.2	1.44	0.34	0.090	115,000	
	6.2	2.33	0.38	0.079	128,000	
	8.5	3.66	0.43	0.070	143,000	
					127,000	1,850
Cyclorubber prepared with tin tetrachloride	2.00	1.59	0.80	0.070	36,000	
	4.13	3.39	0.82	0.052	38,000	
	6.14	5.10	0.83	0.044	40,000	
	7.97	6.77	0.85	0.039	42,000	
					39,000	570

Table XXV gives the experimental results, and Table XXVI gives a comparison of the molecular weights obtained by the two different methods.

TABLE XXVI

AVERAGE DEGREES OF POLYMERIZATION OF MASTICATED, OXIDIZED AND CYCLIZED RUBBERS ACCORDING TO THE METHOD OF LIMITS AND ACCORDING TO THE s VALUES

Product	lim (p/c)	Average degree of polymerization from the lim (p/c) $c \to 0$	Average degree of polymerization from the s values
Masticated rubber (technical)			
Easily soluble fraction	0.30	1200	1350
Difficultly soluble fraction	0.17	2100	2300
Masticated rubber			
Easily soluble fraction	0.35	1050	1350
Difficultly soluble fraction	0.37	1000	1100
Crepe rubber I oxidized by potassium permanganate	0.24	1500	1950
Crepe rubber II oxidized by potassium permanganate			
Easily soluble fraction	0.28	1300	1250
Difficultly soluble fraction	0.21	1700	1850
Cyclorubber (prepared with tin tetrachloride)	0.78	460	570

DETERMINATION OF THE K_m AND $K_{equiv.}$ VALUES OF MASTICATED, OXIDIZED AND CYCLIZED RUBBERS

Viscosity measurements of various rubbers were carried out in the range of sol solutions. The results are recorded in Table XXVII.

The η_{sp}/c values of these rubbers at 20° C and 60° C are, within experimental errors, approximately the same.

The K_m and $K_{equiv.}$ values of various kinds of rubber were determined from the viscosity numbers and from the average degrees of polymerization calculated from the s values. The results are recorded in Table XXIX.

Masticated rubbers and rubbers oxidized by potassium permanganate have approximately the same K_m values, which are about one-third smaller than those of the corresponding untreated polyprenes. As a consequence, solutions of masticated rubbers are less viscous than are those of unmasticated rubbers. This in turn led to the earlier assumption that masticated rubbers are considerably degraded by the action of atmospheric oxygen[76]. This assumption was based on the fact that, when rubber is masticated in the absence of air, the viscosity of a solution of the masticated rubber is not so different from the viscosity of a corresponding solution of the original rubber as is the viscosity of a solution of the same rubber masticated in open air[77]. Likewise, the elasticity of rubber is relatively little changed by mastication in the absence of air. According to previous investigations, rubber masticated in the presence of air still has a relatively high molecular weight. The lowering of the viscosity depends, therefore, only partly on the fact that rubber is degraded by mastication; and the phenomenon is to be ascribed also in part to the fact that mastication increases considerably the branching of the macromolecules.

In view of these facts, the mastication process, both in the presence and absence of air, should be investigated anew. In addition, a study must be made of the

TABLE XXVII

VISCOSITY MEASUREMENTS OF MASTICATED, OXIDIZED, AND CYCLIZED RUBBERS IN TOLUENE AT 20° C

Product	Concentration c (g. per l.)	η_r	η_{sp}/c
Masticated rubber (technical)	1.52	1.166	0.109
Easily soluble fraction	1.50	1.166	0.111
Difficultly soluble fraction	0.980	1.166	0.169
	1.10	1.183	0.167
Masticated rubber	1.67	1.217	0.130
Easily soluble fraction	1.65	1.210	0.128
Difficultly soluble fraction	1.36	1.126	0.093
	1.32	1.119	0.090
Crepe rubber I oxidized by potassium permanganate	0.664	1.092	0.138
	0.728	1.101	0.139
Crepe rubber II oxidized by potassium permanganate			
Easily soluble fraction	0.800	1.088	0.110
	0.760	1.081	0.106
Difficultly soluble fraction	0.832	1.124	0.149
	0.636	1.094	0.148
Cyclorubber (prepared with tin tetrachloride)	4.98	1.104	0.021
	4.72	1.101	0.022

TABLE XXVIII

DETERMINATION OF THE η_{sp}/c VALUES OF SOLUTIONS OF MASTICATED, OXIDIZED, AND CYCLIZED RUBBERS AT 20° C AND 60° C

Product	η_{sp}/c at 20° C	η_{sp}/c at 60° C	$\frac{\eta_{sp}/c \text{ at } 60° \text{ C}}{\eta_{sp}/c \text{ at } 20° \text{ C}}$
Masticated rubber (technical)	0.109	0.107	0.98
Easily soluble fraction	0.111	0.103	0.93
Difficultly soluble fraction	0.169	0.156	0.92
	0.167	0.157	0.94
Masticated rubber	0.130	0.132	1.02
Easily soluble fraction	0.128	0.130	1.02
Difficultly soluble fraction	0.093	0.093	1.00
	0.090	0.090	1.00
Crepe rubber I oxidized by potassium permanganate	0.138	0.127	0.92
	0.139	0.133	0.96
Crepe rubber II oxidized by potassium permanganate			
Easily soluble fraction	0.110	0.110	1.00
	0.106	0.106	1.00
Difficultly soluble fraction	0.149	0.145	0.97
	0.148	0.143	0.97
Cyclorubber (prepared with tin tetrachloride)	0.021	0.022	1.05
	0.022	0.021	0.96

TABLE XXIX

DETERMINATION OF THE K_m AND $K_{equiv.}$ VALUES OF MASTICATED, OXIDIZED, AND CYCLIZED RUBBERS

Product	η_{sp}/c at 20° C	Average degree of polymerization from the s values	No. of chain members	$Km \times 10^4$	$K_{equiv.} \times 10^4$
Masticated rubber (technical)					
Easily soluble fraction	0.110	1350	5400	0.8	0.20
Difficultly soluble fraction	0.168	2300	9200	0.7	0.18
Masticated rubber					
Easily soluble fraction	0.129	1350	5400	1.0	0.24
Difficultly soluble fraction	0.091	1100	4400	0.8	0.21
Crepe rubber I oxidized by potassium permanganate	0.138	1950	7800	0.7	0.18
Crepe rubber II oxidized by potassium permanganate					
Easily soluble fraction	0.108	1250	5000	0.9	0.22
Difficultly soluble fraction	0.148	1850	7400	0.8	0.20
Cyclorubber (prepared with tin tetrachloride)	0.021	571	2280	0.4	0.09

extent to which the addition of an oxidizing agent brings about branching of the macromolecules. The solution of this problem is of technical importance, for rubbers having the same degree of polymerization but considerably differently branched macromolecules presumably would have different physical properties, *e.g.*, different elasticities.

Rubber cyclized by tin tetrachloride is strongly degraded, and it is possible that this degradation is brought about by traces of oxygen. Mojen[78] was able to prove that the autoöxidative degradation of rubber is promoted to an extraordinary extent by the presence of hydrogen chloride.

In earlier investigations, cyclorubbers, which were prepared by treatment of rubber hydrochlorides with zinc, have been described[79]; the molecular weights of a series of hemicolloidal, pulverulent substances which had been prepared under various conditions were determined in benzene by the cryoscopic method[80], and, at the same time, viscosity measurements in this same solvent were carried out[81]. The K_m and $K_{equiv.}$ values obtained in this way were smaller than those

TABLE XXX

DETERMINATION OF THE K_m AND $K_{equiv.}$ VALUES OF CYCLORUBBER AND OF CYCLOGUTTA-PERCHA IN BENZENE[81]

Product	Prepared in	Average degree of polymerization	η_{sp}/c	$K_m \times 10^4$	$K_{equiv.} \times 10^4$
Cyclorubber	Tetralin	37	0.087	2.4	0.60
Cyclogutta-percha	Tetralin	37	0.088	2.4	0.60
Cyclorubber (unfractionated)	Xylene	120	0.155	1.3	0.32
Cyclorubber (ether-soluble)	Xylene	68	0.100	1.5	0.37
Cyclorubber (ether-insoluble)	Xylene	190	0.190	1.0	0.25
Cyclogutta-percha (unfractionated)	Xylene	50	0.105	2.1	0.50
Cyclogutta-percha (ether-soluble)	Xylene	41	0.100	2.4	0.60
Cyclogutta-percha (ether-insoluble)	Xylene	110	0.157	1.4	0.35

of hemicolloidal polyprenes and polypranes prepared by thermal degradation of rubber and gutta-percha (compare Table XXX with Table VII).

According to these results, the molecules of hemicolloidal cyclorubbers, especially those with relatively high molecular weights, become more or less branched by the cyclization reactions.

DETERMINATION OF THE K_m AND $K_{equiv.}$ VALUES OF POLYPRANES

PREPARATION OF THE PRODUCTS

Determinations by the osmotic method of the molecular weights of rubber in solution are carried out only with difficulty, for with increasing degree of purification of a rubber, the sensitivity of the latter to oxygen increases. Because of this, a series of polypranes, including hydrorubber, hydrogutta-percha and hydrobalata, was chosen, and the K_m and $K_{equiv.}$ values of these relatively stable hydrocarbons were determined[82].

Because of the sensitivity of polyprenes, it is difficult to prepare a eucolloidal polyprane. During reduction it is difficult to avoid not only an autoöxidative degradation of a polyprane by traces of atmospheric oxygen, but also thermal degradation, since this reduction must be carried out at elevated temperatures[83].

The reduction of polyprenes to polypranes[84] was carried out under carefully controlled conditions in decalin which had been purified from unsaturated compounds[85]. Raney nickel was the catalyst[86]. It was prepared in the well known

way from a 50 per cent nickel-aluminum alloy[87]. Reduction was carried out in a rotary autoclave[88]. To a 2-3 per cent solution of polyprene in decalin, completely free of oxygen, was added Raney nickel in three times the quantity of the polyprene. This nickel had been kept in decalin in an atmosphere of pure nitrogen, with complete exclusion of air. The mixture was then hydrogenated for several hours at 100-120° C, under a pressure of 250-300 atmospheres of hydrogen. In this way a portion of the reactive double bonds became saturated. When the sensitive allyl groups[12] in the rubber chains were destroyed, the temperature was raised and the hydrogenation was completed by heating for 10 hours at 150-160° C.

To recover the polyprane, the solution was freed of the greater part of the nickel by centrifuging. The solution was then diluted with decalin to lower its viscosity. The decanted solution was dark colored because of colloidally dissolved nickel. To remove the latter, the solution was agitated with a little magnesium oxide until the supernatant liquid was completely clear. The magnesium oxide[89] was removed by centrifuging and filtering. The polypranes were then precipitated from the clear solution by adding acetone, and were purified by solution in

TABLE XXXI

ANALYSES OF HYDROGUTTA-PERCHA, HYDROBALATA AND HYDRORUBBER

Product	Average degree of polymerization	Carbon (percentage)	Hydrogen (percentage)	Ash[90] (percentage)
Hydrogutta-percha	1,100	85.52	14.09	0.39
Hydrobalata	850	86.35	13.60	Ash-free
Hydrorubber				
Easily soluble fraction	800	85.60	14.40	Ash-free
Difficultly soluble fraction	1,450	85.75	14.46	0.14
Hydrorubber (technical)[91]	950	86.08	13.90	0.07
Calculated for $(C_5H_{10})_x$	—	85.63	14.37	—

toluene and reprecipitation by acetone. In this way the last trace of decalin was removed. To obtain a product completely free of ash, the first portions of the precipitates were in most cases discarded, since most of the inorganic components were contained in these portions. By using a reactive catalyst, it was possible to transform the polyprenes into polypranes, as is evident from the analyses recorded in Table XXXI.

Solutions of these completely saturated polypranes did not decolorize solutions of bromine in carbon disulfide, nor did they give any coloration with tetranitromethane.

OSMOTIC MEASUREMENTS OF POLYPRANES

Since polypranes are so insensitive, it is unnecessary to operate either with exclusion of air and light, or in special osmometers, and their molecular weights can be determined relatively easily by osmotic measurements.

The (p/c)-c curves of the different polypranes are not strictly parallel. This is an indication that these hydrocarbons are not true homologous polymers. A further indication of this is the fact that the K_m values of the different polypranes are not exactly the same.

The s values of the various hydrogenation products fall on a straight line on which also lie the s values of the masticated rubbers and the rubbers investigated by Caspari.

TABLE XXXII

OSMOTIC MEASUREMENTS OF HYDROGUTTA-PERCHA, HYDROBALATA AND HODRORUBBER IN TOLUENE AT 27° C

Product	Concentration c (g. per l.)	$p \times 10^3$	$(p/c) \times 10^3$	Specific active volume (s)	Average molecular weight	Average degree of polymerization
Hydrogutta-percha	2.03	0.85	0.42	0.093	72,000	
	4.09	1.74	0.43	0.069	80,000	
	6.15	2.76	0.45	0.056	83,000	
					78,000	1,100
Hydrobalata	2.02	1.06	0.52	0.084	57,000	
	3.97	2.14	0.54	0.063	60,000	
	6.07	3.66	0.61	0.050	58,000	
					58,000	850
Hydrorubber						
Easily soluble fraction	2.10	1.09	0.52	0.082	57,000	
	4.32	2.58	0.58	0.058	56,000	
	8.28	5.09	0.61	0.046	63,000	
					59,000	850
Difficultly soluble fraction	2.20	0.69	0.32	0.099	100,000	
	4.08	1.39	0.34	0.074	103,000	
	6.20	2.36	0.38	0.060	103,000	
	8.12	3.29	0.40	0.052	105,000	
					103,000	1,500
Hydrorubber (technical)	1.60	0.69	0.43	0.100	68,000	
	3.25	1.59	0.49	0.070	65,000	
	5.99	3.39	0.57	0.052	64,000	
					65,000	950

Here too the limiting p/c values as c approaches zero were used for calculating the s values.

Table XXXIII summarizes the molecular weights determined by two different methods.

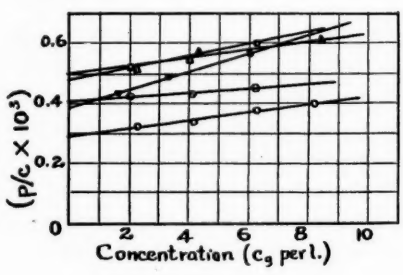


FIG. 13.

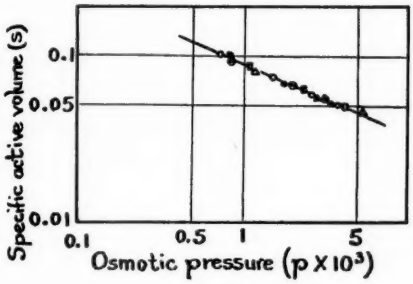


FIG. 14.

FIG. 13.—(p/c)-c Curves of hydrogutta-percha, hydrobalata and hydrorubber in toluene at 27° C.

⊙ Hydrogutta-percha.
□ Hydrobalata.
Hydrorubber:
△ Easily soluble fraction.
○ Difficultly soluble fraction.
● Hydrorubber (technical).

FIG. 14.—Relation between specific volume (s) and osmotic pressure (p) of hydrogutta-percha, hydrobalata and hydrorubber.

⊙ Hydrogutta-percha.
□ Hydrobalata.
Hydrorubber:
△ Easily soluble fraction.
○ Difficultly soluble fraction.
● Hydrorubber (technical).

TABLE XXXIII

Product	$\lim_{c\to 0}(p/c)$	Average degree of polymerization from $\lim_{c\to 0}(p/c)$	Average degree of polymerization
Hydrogutta-percha	0.40	900	1,100
Hydrobalata	0.48	750	850
Hydrorubber			
Easily soluble fraction	0.49	750	800
Difficultly soluble fraction	0.29	1,250	1,500
Hydrorubber (technical)	0.38	950	950

DETERMINATION OF THE K_m AND $K_{equiv.}$ VALUES OF POLYPRANES

Viscosity measurements of these polypranes were carried out in all cases in toluene and in two cases in carbon tetrachloride as well. In agreement with earlier observations[92], the η_{sp}/c values in toluene were about 20 per cent lower than those in carbon tetrachloride.

The temperature effect in solutions of polypranes in toluene is very small, as is the case with rubber solutions, and particularly with solutions of masticated rubber.

The K_m and $K_{equiv.}$ values were determined from the viscosity numbers, and from the average degrees of polymerization were derived from osmotic measurements.

TABLE XXXIV

VISCOSITY MEASUREMENTS OF HYDROGUTTA-PERCHA, HYDROBALATA, AND HYDRORUBBER IN TOLUENE AT 20° C

Product	Solvent	Concentration c (g. per l.)	η_r at 20° C	η_{sp}/c at 20° C	$\frac{\eta_{sp}/c \text{ in toluene}}{\eta_{sp}/c \text{ in } CCl_4}$
Hydrogutta-percha	Toluene	0.932	1.21	0.130	
		0.852	1.110	0.129	0.80
	Carbon tetrachloride	0.764	1.123	0.161	
		0.796	1.128	0.161	
Hydrobalata	Toluene	0.552	1.069	0.125	
		0.700	1.087	0.124	0.85
	Carbon tetrachloride	0.764	1.112	0.146	
		0.764	1.113	0.148	
Hydrorubber					
Easily soluble fraction	Toluene	0.568	1.051	0.089	
		0.596	1.053	0.089	—
Difficultly soluble fraction	Toluene	0.628	1.080	0.127	
		0.564	1.072	0.127	
Hydrorubber (technical)	Toluene	0.784	1.105	0.134	
		0.796	1.105	0.132	—

The K_m and $K_{equiv.}$ values of the polypranes differ considerably. However, on the average they are of the same order of magnitude as those of the corresponding polyprenes. Accordingly there is no essential molecular change during the reduction of polyprenes to polypranes[93]. The $K_{equiv.}$ values are all much lower than the $K_{equiv.}$ values of low-molecular hydrocarbons, which show values of approximately 0.95×10^4. Therefore macromolecules of polypranes are not long unbranched fibres, but have a complicated structure and a complicated shape.

TABLE XXXV

COMPARISON OF THE η_{sp}/c VALUES OF SOLUTIONS OF HYDROGUTTA-PERCHA, HYDROBALATA AND HYDRORUBBER IN TOLUENE AT 20° C AND 60° C

Product	Solvent	η_{sp}/c at 20° C	η_{sp}/c at 60° C	$\frac{\eta_{sp}/c \text{ at } 60° \text{ C}}{\eta_{sp}/c \text{ at } 20° \text{ C}}$
Hydrogutta-percha	Toluene	0.130	0.133	1.02
		0.129	0.134	1.04
Hydrobalata	Carbon tetrachloride	0.161	0.160	0.99
		0.161	0.154	0.96
	Toluene	0.125	0.123	0.99
		0.124	0.123	0.99
	Carbon tetrachloride	0.146	0.084	0.94
		0.148	0.143	0.97
Hydrorubber				
Easily soluble fraction	Toluene	0.089	0.084	0.94
		0.089	0.087	0.98
Difficultly soluble fraction	Toluene	0.127	0.128	1.01
		0.127	0.125	0.98
Hydrorubber (technical)	Toluene	0.134	0.139	1.04
		0.132	0.142	1.08

TABLE XXXVI

DETERMINATION OF THE K_m AND $K_{equiv.}$ VALUES OF HYDROGUTTA-PERCHA, HYDROBALATA AND HYDRORUBBER IN TOLUENE

Product	η_{sp}/c at 20° C	Average degree of polymerization from the s values	No. of chain members	$K_m \times 10^4$	$K_{equiv.} \times 10^4$
Hydrogutta-percha	0.130	1,100	4,400	1.2	0.30
Hydrobalata	0.125	850	3,400	1.5	0.37
Hydrorubber					
Easily soluble fraction	0.089	800	3,200	1.1	0.28
Difficultly soluble fraction	0.127	1,500	5,800	0.9	0.22
Hydrorubber (technical)	0.133	950	3,800	1.4	0.37

THE STRUCTURE OF THE MACROMOLECULES OF RUBBER, GUTTA-PERCHA AND BALATA

COMPARISON OF THE K_m AND $K_{equiv.}$ VALUES OF POLYPRENES AND POLYPRANES

In conclusion, the K_m and $K_{equiv.}$ values of polyprenes and polypranes which were determined in the work described in the present paper are summarized in Table XXXVII.

These K_m and $K_{equiv.}$ values differ considerably. The highest $K_{equiv.}$ values are, as anticipated, those of polyprenes and polypranes, the macromolecules of which

Table XXXVII

Comparison of the True and Apparent Average Degrees of Polymerization of Hydrocarbons of Rubber, Gutta-Percha, Balata and Derivatives of These Substances

Product	Solvent	Average degree of polymerization by the osmotic method	η_{sp}/c	Apparent average degree of polymerization $K_m = 4.24 \times 10^{-4}$ for toluene $K_m = 3.8 \times 10^{-4}$ for CCl_4	Degree of branching (Osmotic average degree of polymerization divided by viscometric average degree of polymerization)	$K_m \times 10^4$	$K_{equiv.} \times 10^4$
Gutta-percha I	Carbon tetrachloride	1900	0.305	700	2.7	1.6	0.40
Gutta-percha II	Carbon tetrachloride	1650	0.265	600	2.7	1.6	0.40
Gutta-percha II	Toluene	1550	0.210	550	2.8	1.4	0.34
Balata I	Toluene	1300	0.165	450	2.9	1.3	0.32
Balata II	Toluene	1450	0.188	500	2.9	1.3	—
Rubber (ether-soluble; treated with alkali by the method of Pummerer)	Toluene	1600	0.126	350	4.6	0.8	0.20
Rubber (treated with aluminum oxide)	Toluene	5100	0.900	2400	2.1	1.7	0.44
Rubber (ether-soluble)							
Easily soluble fraction	Toluene	3600	0.389	1000	3.6	1.1	0.27
Difficultly soluble fraction	Toluene	2700	0.460	1200	2.2	1.7	0.43
Masticated rubber (technical)							
Easily soluble fraction	Toluene	1350	0.110	300	4.5	0.8	0.20
Difficultly soluble fraction	Toluene	2300	0.168	450	5.1	0.7	0.18
Masticated rubber							
Easily soluble fraction	Toluene	1350	0.129	350	3.9	1.00	0.24
Difficultly soluble fraction	Toluene	1100	0.091	250	4.4	0.80	0.21
Rubber I (oxidized by potassium permanganate)	Toluene	1950	0.138	350	5.6	0.7	0.18
Rubber II (oxidized by potassium permanganate							
Easily soluble fraction	Toluene	1250	0.108	300	4.2	0.9	0.22
Difficultly soluble fraction	Toluene	1850	0.148	400	4.6	0.8	0.20
Cyclorubber (prepared with tin tetrachloride)	Toluene	570	0.021	55	10.0	0.4	0.09
Hydrogutta-percha	Toluene	1100	0.130	350	3.1	1.2	0.30
Hydrobalata	Toluene	850	0.125	350	2.4	1.5	0.37
Hydrorubber							
Easily soluble fraction	Toluene	800	0.089	250	3.2	0.9	0.22
Difficultly soluble fraction	Toluene	1500	0.127	350	4.3	1.1	0.22
Hyrorubber (technical)	Toluene	950	0.133	350	2.7	1.4	0.37

have undergone little or no damage by secondary influences. These values are, therefore, of particular service in judging the structure of macromolecules. The lower K_m values of a series of hydrocarbons, as will be explained later (see page 517), are to be ascribed to the fact that these hydrocarbons have undergone changes, branchings or cyclization phenomena in the original macromolecules, as a result of secondary reactions These effects are manifest in a shortening of the elongated molecules, with consequent lowering of the viscosity numbers and therefore of the K_m values as well (according to Equation 1b, page 475).

The maximum $K_{equiv.}$ values of polyprenes and polypranes, are of approximately the same magnitude, particularly those of gutta-percha and balata and their hydrogenation products. Therefore the same relations between the average degree of polymerization and viscosity numbers hold true of these very high molecular products, regardless of whether their hydrocarbons are saturated or unsaturated. This was first observed in hemicolloidal polypranes and polyprenes[94], and later in squalenes and hydrosqualenes[95]. According to this, only the length of molecule and not the inner structure is of decisive influence on the specific viscosity of solutions of a homopolar substance. The introduction of double bonds into saturated hydrocarbons, which changes the chemical properties of the latter greatly, have therefore no appreciable influence on their solvation, for otherwise, squalenes and hydrosqualenes would not have the same viscosity numbers.

Furthermore the K_m values of gutta-percha and balata on the one hand and of rubber on the other are not very different. Accordingly the elongated macromolecules of different hydrocarbons with the same average degrees of polymerization in solution must be of the same length. This is surprising for, in the solid state, these polyprenes show different physical properties. At ordinary temperatures, gutta-percha and balata are fibrous and have little elasticity, whereas rubber is highly elastic. Therefore at one time it seemed reasonable to assume that the macromolecules of these polyprenes have fundamentally different structures, with the same differences in the extent of branching as are found, for example, in starch and cellulose[96]. However, according to previous investigations, this cannot be so, for the K_m values of these polyprenes are approximately the same. Probably rubber and gutta-percha are *cis*-isomers[97], because, after reduction, the hydrogenation products of both polyprenes show no differences in physical properties. This view is generally accepted today. The only question still unanswered is to which of the two hydrocarbons is to be ascribed the *cis*-form and to which is to be ascribed the *trans*-form[98].

More recently, various investigators have attempted to explain the elasticity of rubber on the basis that rubber is composed of tightly coiled molecules, and that these become extended during elastic stretching[99]. This is in harmony with the fact that rubber crystallizes when stretched[100], and also calculations by Kohn[101] support this view.

On the other hand, at variance with this assumption is the discovery that the molecules of elastic rubber in solution are of approximately the same length as those of only slightly elastic gutta-percha and balata of the same average degree of polymerization, since the K_m values of the two polyprenes are not very different.

Likewise, the viscosity-temperature relations of solutions of each of these two hydrocarbons are the same. It therefore remains to be proved whether or not elasticity is to be explained in some other way; for example, that it is related in some manner to a change in orientation and form of the crystallites or of the bundles of molecules, rather than to a change in form of the individual macromolecules[102]. In any case, elasticity is in some way related to a restricted range

of temperature. As well known, rubber becomes inelastic when cooled, and gutta-percha and balata become more elastic when warmed. Also, gutta-percha and balata show improved elastic properties when vulcanized[103], but it is not yet clear whether vulcanization lowers the melting point or whether the branchings or network formation of the fibre molecules brought about by vulcanization lead to an increase in elasticity.

Extrapolation of the Viscosity Law

In earlier investigations[104] it was assumed that the viscosity law of linear macromolecular substances holds true also of mesocolloidal and eucolloidal polypranes and polyprenes and, therefore, that it is possible to calculate the average molecular weights and the average degrees of polymerization of these members from viscosity measurements with the aid of the constant 3×10^{-4} found for hemicolloidal substances. This seemed quite reasonable at the time, since approximately the same constant of crude rubber was obtained from the measurements of Caspari (see Tables VII and IX).

But according to the foregoing investigations, this method leads to incorrect results, for the average degrees of polymerization of polyprenes and polypranes, obtained from osmotic measurements, are much higher than had been assumed previously on the basis of viscosity measurements; in fact they are double to five-fold as great. In Table XXXVII the apparent average degrees of polymerization, calculated from viscosity measurements, are compared with the true average degrees of polymerization as obtained from osmotic measurements.

Formerly doubt was repeatedly expressed that the well-defined relations between the viscosity numbers and chain lengths of low-molecular compounds and hemicolloids could be used for calculating the chain lengths of the fibre molecules of mesocolloids and eucolloids. For, at that time, it was the opinion that too high values for the chain lengths and molecular weights would thus be obtained. Fikentscher and Mark[105] for example, and Eisenschitz[106] as well, assumed that the specific viscosity of a solution does not change in proportion to the increase in molecular weight, but rather increases as the square of the molecular weight and chain length. In reality, exactly the opposite is true of rubber and synthetic polymers[107]. The molecular weights determined by the viscometric method are much smaller than those determined by the osmotic method.

The viscosity law of fibre molecules has been demonstrated to be valid for a series of homogeneous substances[108], although only for substances with relatively small numbers of chain members. This has been confirmed also for hemicolloidal polyethylene oxides and polyesters[108]. It was proved that, with these latter compounds, the law holds true of low numbers ($n=100$) up to those with a chain-length number of $n=1600$. In the case of cellulose derivatives, mannans and mannan nitrate, it was proved that the law is valid over particularly wide ranges[108]. A summary of the important results obtained in earlier investigations is shown in Table XXXVIII.

On the basis of these investigations, it seemed at one time justifiable to assume that the viscosity law is applicable to all homopolar substances with fibre molecules in homopolar solvents and, therefore, that it is possible to determine the length of fibre molecules in solution from viscometric measurements.

The validity of the law in the cases cited above led further to the hypothesis that fibre molecules are elongated in solution, and therefore have the same form as in the solid state, except that the regular vibrations of the fiber molecules are greater in solution than they are in the solid state.

Table XXXVIII

Validity of the Viscosity Law for Various Series of Homologous Polymeric Compounds

Product	Literature	Method of determining molecular weight	Average degree of polymerization	No. of chain members	$K_m \times 10^4$	$K_{equiv.} \times 10^4$
Low-molecular hydrocarbons	Staudinger and Staiger, *Ber.* **68**, 707 (1935)	Exact molecular weight by synthesis	—	27-35	—	1.06 in CCl_4 0.96 in C_6H_6
Low-molecular esters and acid anhydrides	Staudinger and Schwalenstöcker, *Ber.* **68**, 727 (1935); Staudinger and Moser, *Ber.* **69**, 208 (1936)	Exact molecular weight by synthesis	—	25-50	—	1.04 in CCl_4 0.90 in C_6H_6
Polyoxymethylene	Staudinger and Kern, "Die hochmolekularen organischen Verbindungen, Kautschuk und Cellulose", Springer, Berlin, **1932**, p. 234	Determination of end groups cryoscopically	10-100	20-200	0.8 in $HCONH_2$	0.4 in $HCONH_2$
Polyethylene oxide dihydrate	Fordyce and Hibbert, *J. Am. Chem. Soc.* **61**, 1912 (1939)	Determination of end groups cryoscopically and by synthesis	100-186	300-560	0.83 in CCl_4 and dioxan	0.28 in CCl_4 and dioxan
Polyhydroxydecanic acid	Kraemer and van Natta, *J. Phys. Chem.* **36**, 3186 (1932)	Determination of end groups cryoscopically and by ultracentrifuging	37-148	400-1630	—	1.1 in $Cl_2HCCHCl_2$
Methyl polyhydroxyundecanate	Unpublished experiments of O. Nuss	Determination of end groups cryoscopically	4-27	50-320	—	0.93 in C_6H_6
Polyesters of hexandiol and sebacinic acid	Staudinger and Schmidt, *J. prakt. Chem.* [2] **155**, 129 (1940)	Determination of end groups cryoscopically	—	95-350	—	0.93 in C_6H_6
Mannan and mannan nitrate	Husemann, *J. prakt. Chem.* [2] **155**, 241 (1940)	Osmotically	165-1340 45-1550	820-6700 230-7700	14.8 in water 8.8 in acetone	2.9 in water 1.7 in acetone
Cellulose acetate	Staudinger and Schulz, *Ber.* **68**, 2320 (1935); Staudinger and Mohr, *Ber.* **70**, 2296 (1938)	Determination of end groups* osmotically	20-780	100-3900	6.3 in *m*-cresol 5.3 in $CHCl_3$	1.3 in *m*-cresol 1.1 in $CHCl_3$
Cellulose nitrate	Unpublished experiments of K. Eder; Staudinger and Daumiller, *Ann.* **529**, 219 (1937)	Osmotically	210-1600	1050-8000	11 in acetone	2.0 in acetone
Ethyl cellulose	Staudinger and Reinecke, *Ann.* **535**, 47 (1938)	Osmotically	90-270	450-1300	12 in $CHCl_3$ 11 in *m*-cresol	2.05 in $CHCl_3$ 1.0 in *m*-cresol

* For products having degrees of polymerization of 20-60.

On the basis of this assumption, viscosity measurements give an indication of the lengths of the fibre molecules of polyprenes and polypranes in solution. According to this, the length of the macromolecules of these hydrocarbons corresponds to only one-half to two-tenths of the isoprene residues which are actually present in the particular macromolecules. The length of the chains of cyclorubber is only about one-tenth that of the isoprene residues which the molecules contains.

The Forms of the Macromolecules of Polyprenes and Polypranes in Solution

The further question then arises as to the manner in which this shortening of the macromolecules of polyprenes and polypranes takes place. This subject has already been discussed in connection with synthetic polyvinyl derivatives, including polyvinyl chlorides[109], polyvinyl acetates, polyacrylic esters and polymethacrylic esters[110]. In the case of these compounds too, the $K_{equiv.}$ values are only one-half to one-ninth as great as the $K_{equiv.}$ values of low-molecular compounds with fibre molecules (0.95×10^{-4}) (see Table XXXIX).

In earlier investigations the idea was advanced[111] that this difference can be explained in the following way. If it is assumed that the macromolecules of polyprenes and polypranes, as well as those of synthetic polyvinyl derivatives, are composed of unbranched fibre molecules, the fibre molecules of polyvinyl derivatives in solution must have different forms from those of polyprenes and polypranes, to which the viscosity law applies; in fact in contrast to substances with elongated fibre molecules in solution, as those in Table XXXVIII, they must be considerably bent. A coiling or a high degree of bending of fibre molecules in solution has, as a matter of fact, been suggested already by other investigators, as mentioned earlier (see page 511).

At variance with the idea that there are two groups of high polymers whose unbranched fibre molecules in solution have different forms are the following observations. Balata and gutta-percha crystallize well from their solutions[112] and, as already mentioned, this ready crystallization can hardly be reconciled with a pronounced coiling or bending of the fibre molecules while in solution. Furthermore balata and gutta-percha, and also their hydrogenation products, have approximately the same K_m values (see Table XXXVII). If the fibre molecules of these hydrocarbons were coiled or bent in solution, and the deviation from the viscosity law were attributable to this, the bending of the fibre molecules of an unsaturated hydrocarbon in solution would be expected to be different from the bending of the fibre molecules of a saturated hydrocarbon. Then again, the temperature relation, *e.g.*, the ratio of the specific viscosity at 60° C to that at 20° C, for all these substances is approximately the same as that of low-molecular substances with fibre molecules[113] and of polyesters[114], to which the viscosity law applies.

It seems more probable that the deviation from the viscosity law shown by polypranes and polyprenes is explainable by the fact that their macromolecules are greatly elongated, with branchings of unknown character. In this way it is possible also to explain in a simple way the deviations of the K_m and $K_{equiv.}$ values of polyprenes by differences in the extent of branching. Furthermore it is possible, by assuming that the molecules are in an elongated state even in solution, to obtain an idea of the extent of these branchings by the ratio of the average degree of polymerization, determined osmotically, to the chain length, determined viscometrically.

TABLE XXXIX

INVALIDITY OF THE VISCOSITY LAW FOR VARIOUS HOMOLOGOUS POLYMERIC SERIES

Product	Literature	Method of determining molecular weight	Degree of polymerization	No. of chain members	$K_m \times 10^4$	$K_{equiv.} \times 10^4$	$\frac{0.95}{K_{equiv.}}$ = extent of branching
Polyvinyl chloride	Staudinger and Schneiders, *Ann.* **541**, 151 (1939)	Osmotically	1,000-2,500	2,000- 5,000	1.05-0.54 in tetrahydrofuran	0.52-0.27 in tetrahydrofuran	1.8-3.5
Polyvinyl acetate	Staudinger and Warth, *J. prakt. Chem.* [2] **155**, 261 (1940)	Osmotically	850-3,650	1,700- 7,300	0.52-0.25 in acetone	0.26-0.12 in acetone	3.6-7.9
Methyl polyacrylate	Staudinger and Warth, *J. prakt. Chem.* [2] **155**, 261 (1940)	Osmotically	850-3,750	1,700- 7,500	0.45-0.31 in acetone	0.22-0.16 in acetone	4.3-5.9
Methyl polymethacrylate	Staudinger and Warth, *J. prakt. Chem.* [2] **155**, 261 (1940)	Osmotically	250-2,600	500- 5,200	0.56-0.19 in acetone	0.27-0.10 in acetone	3.5-9.5
Polystyrene	Staudinger and Schulz, *Ber.* **68**, 2331 (1935)	Osmotically	800-6,000	1,600-12,000	0.4 -1.25 in toluene	0.2 -0.63 in toluene	4.7-1.4
Polyprene	—	—	1,300-5,100	5,200-20,000	0.8 -1.7 in toluene	0.2 -0.42 in toluene	4.7-2.3

This extent of branching is likewise equal to the ratio 0.95×10^{-4}, *i.e.*, of the $K_{equiv.}$ constant of low-molecular substances to the experimental $K_{equiv.}$ values:

$$\text{Extent of branching} = \frac{\text{degree of polymerization (osmotic)}}{\text{degree of polymerization (viscometric)}} = \frac{0.95 \times 10^{-4}}{K_{equiv.}\text{ (exptl.)}}$$

Therefore in the case of polyprenes with strongly branched macromolecules, the ratio of the isoprene residues from which the macromolecules are built up to the chain-forming isoprene residues is greater than it is in the case of polyprenes with less branching. In the case of substances with unbranched fibre molecules, this ratio is equal to 1.

In favor of the hypothesis that the macromolecules of polyprenes are branched is the observation that the K_m and $K_{equiv.}$ values of polybutadiene[115], the macromolecules of which are certainly branched as judged by chemical investigations, are of approximately the same size as those of the natural products. Furthermore it has already been shown by chemical methods that polyesters, to which the viscosity law of fibre molecules does not apply, are branched[116].

In the case of polyprenes and polypranes, it is very difficult to obtain a direct proof of branching from the size of the macromolecules. The idea of branching is in harmony with earlier chemical observations on the structure of rubber, for Pummerer, Ebermayer and Gerlach[117], who studied the decomposition of rubber by the action of ozone under specially controlled conditions, were able to

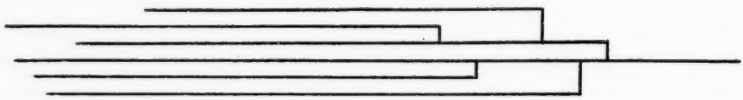


FIG. 15.

find only 90 per cent of the calculated amount of cleavage products which should have been recovered if rubber were composed of long, simply constructed, unbranched fibre molecules[118].

The ready crystallization of balata and gutta-percha is not incompatible with the hypothesis of branching, for polyesters, which chemical investigations have shown to be branched, are crystalline[119]. The crystallization of balata and gutta-percha is explainable on the assumption that the side chains in the branched macromolecules are greatly elongated. If so, it is possible that they lie parallel to the main chains and do not hinder crystallization, as shown diagrammatically in Figure 15.

On this basis the macromolecules of polyprenes and polypranes are comparable to those of cellulose rather than to those of starch[120], even if the extent of branching in starch is much greater than it is in polyprenes and polypranes. Such a structure of polyprene molecules is not impossible, because rubber, gutta-percha and balata are not by nature substances of definite structural form, as is cellulose. There is still the possibility that the differences between rubber on the one hand and gutta-percha and balata on the other hand depend on differences in the character of the branching of their macromolecules, and not merely on a state of *cis*- and *trans*-isomerism.

Homologous Polymeric Series of Polyprenes and Polypranes

The products shown in Table XXXIX, the average molecular weights of which cannot be calculated from the K_m constants obtained by viscosity measurements

of low-molecular compounds, and the $K_{equiv.}$ values of which deviate through a relatively wide range, show great differences among themselves. In a series of polyvinyl chlorides[121], polyvinyl acetates, polyacrylic esters and polymethacrylic esters[122], the $K_{equiv.}$ values decrease regularly with increase in the average degree of polymerization. It is possible, therefore, that the macromolecules of these products are not branched, and that there is a different relation between viscosity and chain length from that of the substances shown in Table XXXVIII. Of course, here too, it is possible that, with increase in the chain length, the number of branchings in the elongated macromolecules increases.

If the first assumption is correct, high-molecular and low-molecular members of the polyvinyl derivatives mentioned would be homologous polymeric compounds, differing only in the lengths of their chains. This would not be true if the second assumption is correct, *viz.*, that macromolecules of relatively high-molecular substances are more extensively branched than those of relatively low-molecular members of the same series. This is the case of polystyrenes prepared at different temperatures[123]. These results are of significance only if it is assumed that the products obtained under different conditions are not in the true sense homologous polymeric members, for the macromolecules of the products obtained at higher temperatures have relatively small K_m values and, therefore, are more extensively branched than those prepared at lower temperatures.

The problem of the molecular structure of rubber, gutta-percha, and balata could be investigated more thoroughly by preparing various members of the homologous series of polyprenes and polypranes, making osmotic and viscometric measurements of these products, and determining whether the $K_{equiv.}$ values increase progressively with decrease in the average degree of polymerization. This investigation has been neglected heretofore because it has been assumed that it would be extremely difficult to prepare members of an homologous series of polyprenes and polypranes of different average molecular weights. As a matter of fact the view has been repeatedly expressed that polyprenes which are formed by degradation of rubber and gutta-percha under various conditions are low-molecular members of this homologous polymeric series[124]. However, as has already been ponited out[14], it is not quite certain whether this view is correct, for, when rubber and gutta-percha are degraded thermally, there is probably not only a cleavage of the fibre molecules into shorter fragments, but also further changes in the macromolecules as a result of cyclization or other secondary reactions, wholly independent of any oxidation caused by traces of atmospheric oxygen. Accordingly it is very difficult to prepare an homologous series of polyprenes and, therefore, of products the macromolecules of which have the same fundamental structure and differ only in their chain lengths. This is true also of polypranes of different degrees of polymerization which are formed by reduction of various polyprenes. For the same reason the members described earlier are perhaps not, in the strict sense, homologous polymers.

At this time, the opportunity should be taken to point out that, up to the present time, it has been quite certain only in a few cases that macromolecular compounds of different average degrees of polymerization which are composed of the same fundamental unit structures, are actually homologous polymers. Among natural substances, the products which are formed by decomposition of crude cellulose by dilute acids[125], and which have different average degrees of polymerization, are members of an homologous series of polymers; for the lower members of the series are formed from the original macromolecules of cellulose by the splitting off of compounds of a more or less glucoside nature, without any changes in the macromolecules[126].

Among synthetic products, there are homologous polymeric series of polyoxymethylenes, polyethylene oxides and polyesters[126]; in other words, substances of different average degrees of polymerization and of different average degrees of condensation, yet with macromolecules of the same structure.

Not all polymerized and polycondensed products are homologous polymers; *e.g.*, δ-polyoxymethylenes are, in the structure of their fibre molecules, somewhat different from α-, β- and γ-polyoxymethylenes[127]. Likewise, in the condensation of hydroxy acids, not only are condensation products with simple fibre molecules formed, but also members with branched molecules[114] which are not homologous polymers. In the case of many vinyl compounds, it is still an open question whether, by polymerization under various conditions, homologous polymers, *i.e.*, substances having macromolecules of the same structure but of different chain lengths, are always formed. This question can be answered only by further investigations. According to experimental material which is available at the present time, the viscosity law is valid in every case in which it has been possible to prove that fibre molecules are strictly homologous polymers.

Branching in the Macromolecules of Rubber

Although the question of the structure of macromolecules of natural polyprenes and polypranes has not yet been answered in any certain way, it has been proved in past investigations that the macromolecules of different types of rubber do not have similar structures, but differ from one another in the extent of branching. Whether branched or not branched, the elongated molecules of rubber are united by oxygen bridges, so there is a further branching of the macromolecules. This is also the case when, by a reaction which corresponds to a cyclization into a polyprene molecule[128], two or more macromolecules of the polyprene combine. Such processes can take place by the action of light and oxidizing agents and also at elevated temperatures. The formation of these branchings is induced by cyclizing agents, such as tin tetrachloride. This is the reason why rubbers which have been degraded by oxidizing agents, and masticated rubbers as well, are not, as once believed, low-molecular members of a homologous series of rubber polymers; these reaction products which are formed from different rubbers differ from the original crude rubber not only by the lengths of their chains, but also by the extent of the branching of their macromolecules. For this reason, it is not justifiable to draw conclusions as to the extent of the decomposition of masticated rubbers and of rubbers which have been acted upon by oxygen by changes in their viscosity numbers, for the K_m values of the products obtained in this way are different from those of the original crude rubber. Accordingly a masticated rubber may, in spite of its relatively small viscosity number, still have a relatively high molecular weight.

It is quite possible that the technical importance of mastication is due to the fibre molecules of rubber becoming more or less linked together by oxygen bridges, with the result that extensively branched macromolecules are formed. In spite of a high degree of polymerization, these macromolecules have a relatively short chain length and, therefore, these products are much more plastic than are the corresponding unmasticated rubbers. However, in spite of the shorter length of its chains, masticated rubber has valuable technical properties, since it is very highly polymerized.

Further investigations of the size and shape of macromolecules of rubber, and of the changes brought about by mastication is of importance from a technical

point of view, for the valuable physical properties of these materials, particularly their elasticity, are related in some still unexplained way to the size and shape of the macromolecules[129]. These factors certainly must be studied more thoroughly before it is possible to express any opinion as to the causes of elasticity.

Up to the present time, only one fact seems to be fairly certain, *viz.*, that the elasticity of rubber is a macromolecular property; for highly degraded, hemicolloidal polyprenes and polypranes do not possess any elastic properties. To what extent the double bonds of rubber play a part in the elastic properties will be shown by an exact comparison of the properties of rubbers and the polymerically analogous hydrorubbers[130]. It is to be hoped that it will be possible to gain a deeper insight, by chemical means, into the problem of elasticity by studying the elastic properties of homologous polyprenes and polypranes of the same degree of branching, and by an investigation of substances of different degrees of branching but of the same average degree of polymerization.

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REFERENCES

[1] Special attention is called once more to this systematic procedure, for the idea occurs repeatedly in the literature that the constitution of highly polymeric substances, including rubber, can be explained on the basis of roentgenographic investigations. Actually, however, no conclusions can be drawn as to characteristic structure and size of macromolecules from investigations of this kind.

[2] Plummerer, Nielsen and Gündel, *Ber.* **60**, 2167 (1927).

[3] Staudinger, Asano, Bondy and Singner, *Ber.* **61**, 2575 (1928); Pummerer, Andriessen and Gündel, *Ber.* **62**, 2628 (1929); Pummerer, *Kautschuk* **5**, 129 (1929).

[4] Meyer and Mark, *Z. angew. Chem.* **41**, 935 (1928); *Ber.* **61**, 1945 (1928).

[5] Staudinger and Fritschi, *Helv. Chim. Acta* **5**, 785 (1922); *Ber.* **57**, 1203 (1924).

[6] Staudinger, *Helv. Chim. Acta* **13**, 1324 (1930); Staudinger and Feist, *Helv. Chim. Acta* **13**, 1361 (1930); Staudinger and Leupold, *Ber.* **67**, 308 (1934); Staudinger, *Kolloid-Z.* **54**, 129 (1931).

[7] Staudinger and Leupold, *Ber.* **67**, 304 (1934).

[8] McBain and Scott, *Ind. Eng. Chem.* **28**, 470 (1936).

[9] With respect to the sensitivity of rubber to oxygen, see Staudinger and Leupold, *Ber.* **63**, 730 (1930).

[10] Actually larger percentages of oxygen are necessary to degrade a polyprene to one-half its average degree of polymerization. See Staudinger and Leupold, "Die Hochmolekularen Organischen Verbindungen, Kautschuk and Cellulose", Springer, Berlin, **1932**, p. 414.

[11] It should be noted that the reduction must be carried out in solution, and that polyprenes of high degrees of polymerization must be reduced in much more dilute solutions than polyprenes of lower degrees of polymerization, for, as is known, the homologous polyprenes of a given concentration increase greatly with increase in degree of polymerization.

[12] This general property of allyl groups has been pointed out in various publications. See, for example, Staudinger and Rheiner, *Helv. Chim. Acta* **7**, 23 (1924); Staudinger, *Ber.* **57**, 1203 (1924); *Kolloid-Z.* **54**, 129 (1931); Staudinger *et al.*, *Helv. Chim. Acta* **13**, 1334 (1930). More recently Schmidt has taken this point of view (*Z. physik. Chem.* [A] **159**, 337 (1932)).

[13] Staudinger, *Helv. Chim. Acta* **13**, 1324 (1930); Staudinger and Feist, *Helv. Chim. Acta* **13**, 1361 (1930); Staudinger and Leupold, *Ber.* **67**, 308 (1934); Staudinger *Kolloid-Z.* **54**, 129 (1931).

[14] In the earlier works, the hemicolloidal and mesocolloidal polyprene members which were obtained by thermal degradation of rubber and gutta-percha were regarded as lower members of the homologous polymeric series. See Staudinger and Bondy, *Ann.* **468**, 1 (1929). However, according to work described later in the present paper, this is not exactly correct, since, when the macromolecules of eucolloidal polyprenes are cracked, cyclization of some other changes in the macromolecules may take place.

[15] Staudinger and Leupold, *Ber.* **67**, 304 (1934).

[16] Staudinger and Mojen, *Kautschuk* **12**, 121 (1936).

[17] Staudinger and Nodzu, *Helv. Chim. Acta* **13**, 1350 (1930).

[18] Staudinger and Bondy, *Ber.* **63**, 734 (1930); Staudinger, Ber. **63**, 921 (1930); *Kautschuk* **6**, 153 (1930); Staudinger and Bondy, *Ann.* **488**, 127 (1931).

[19] Staudinger, *Cellulosechemie*, Dec. **1940**.

[20] For the experimental procedure used in obtaining these measurements, see Staudinger and Leupold, *Ber.* **67**, 304 (1934), and page 504 of the present paper.

[21] Staudinger and Leupold, *Ber.* **63**, 730 (1930).

[22] New unpublished experiments.

[23] The K_m values of degraded polyprenes and polypranes of a degree of polymerization of 250 are still unknown. First of all the molecular weights must be determined osmotically.
[24] Meyer and Mark, *Ber.* **61**, 1935 (1928).
[25] For the distinction between micellar weight and molecular weight, see Staudinger, "Organische Kolloidchemie", Vieweg, Braunschweig, **1940**, p. 103.
[26] Staudinger and Schultz, *Ber.* **68**, 2336 (1935).
[27] Ostwald, *Kolloid-Z.* **49**, 60 (1929). The following statement of Ostwald is not clear, since macromolecules, like the molecules of low-molecular substances, do not differ in size. "After all, there are, naturally borderline transitions between molecular and micellar weights. The most important case is that of so-called eucolloids, *i.e.*, substances the particles of which owe their colloidal dimensions to the aggregation of an extremely large number of atoms by primary valence forces, and the dimensions of which particles change only with changes in these strongest affinities. To this group belong, for example, the primary particles of proteins, although the present author believes it probable that, in ordinary protein sols, these primary particles are aggregated, chiefly through weaker forces, to secondary particles, which, for their part, may change greatly in size, state of solvation, etc. In this case the transition between micellar and molecular weights is of particular significance with extremely dilute sols, in that the secondary particles when in extremely dilute form, frequently (although not necessarily) disperse spontaneously to the smallest individual units, which are held together only by primary valences. In such cases the molecular weight appears to be the limiting value of the micellar weight in theoretically infinite dilution of the system. From this point of view, the present author naturally raises no objection if one speaks of the "molecular weight" of a sol in the sense of a limiting value of the variable micellar weight, especially in the case of eucolloids."
[28] Dobry, *J. chim. phys.* **32**, 50 (1935); *Bull. soc. chim.* **2**, 1882 (1935).
[29] Schulz, *Z. physik. Chem.* **176A**, 317 (1936).
[30] Schulz, *Z. physik. Chem.* **184A**, 30 (1939).
[31] Caspari, *J. Chem. Soc.* **105**, 2139 (1914). This calculation was made by Schulz (*Z. physik. Chem.* **158A**, 243 (1932).
[32] Meyer and Mark, *Ber.* **61**, 1945 (1928).
[33] Kroepelin and Brumshagen, *Ber.* **61**, 2441 (1928); Kroepelin, *Kolloid-Z.* **47**, 294 (1929).
[34] Busse, in "The Chemistry and Technology of Rubber", Edited by Davis and Blake, Reinhold Publishing Corp., New York, **1937**, p. 231, 232; Svedberg and Pedersen, "Die Ultrazentrifuge", Steinkopff, Leipzig, **1940**, p. 386.
[35] Staudinger, "Organische Kolloidchemie", Vieweg, Braunschweig, **1940**, p. 54-55.
[36] Staudinger and Leupold, *Helv. Chim. Acta* **15**, 222 (1932); Staudinger and Mojen, *Kautschuk* **12**, 121 (1936).
[37] Staudinger and Staiger, *Ber.* **68**, 707 (1935).
[38] Staudinger, Geiger, Huber, Schaal and Schwalbach, *Helv. Chim. Acta* **13**, 1334 (1930); Staudinger and Nodzu, *Helv. Chim. Acta* **13**, (1930); Staudinger, Bondy, and Leupold, "Die Hochmolekularen Organischen Verbindungen: Kautschuk and Celluose", Springer, Berlin, **1932**, pp. 396, 407; Staudinger and Bondy, *Ber.* **63**, 734 (1930).
[39] Staudinger and Bondy, *Ann.* **468**, 41 (1929).
[40] Caspari, *J. Chem. Soc.* **105**, 2139 (1914).
[41] Staudinger and Heuer, *Z. physik. Chem.* **171A**, 129 (1934).
[42] Staudinger and Sorkin, *Ber.* **70**, 1993 (1937).
[43] Staudinger and Mojen, *Kautschuk* **13**, 17 (1937).
[44] It should be noted that, in Equation 3, the concentration is expressed in base moles $c_{(gm/liter)}$ and not in $c_{(g/liter)}$.
[45] Staudinger, "Die Hochmolekularen Organischen Verbindungen: Kautschuk und Cellulose", Springer, Berlin, **1932**, p. 442.
[46] Busse, in "The Chemistry and Technology of Rubber", Edited by Davis and Blake, Reinhold Publishing Corp., New York, **1937**, p. 231, 232.
[47] The $[\eta]$ values of Kraemer and Lansing are 10 times as great as the η_{sp}/c values of the present authors. Kraemer and Lansing call the $[\eta]$ values "intrinsic viscosities", and give concentrations in grams per 100 cc. of solution.
[48] The viscosity of rubber in ether is smaller than that of rubber in benzene, since ether is a poorer solvent for rubber than is benzene. As dmonstrated in earlier work, relatively poor solvents give solutions of relatively low viscosity; cf. Staudinger and Heuer, *Z. physik. Chem.* **171A**, 129(1934). The very low K_m values of Kraemer and Lansing are not, however, fully explained in this way.
[49] Dufraisse, *Rev. gén. caoutchouc* **8**, No. 71, 9 (1931).
[50] Clark, *Ind. Eng. Chem.* **18**, 1131 (1926).
[51] von Susich and Hopff, *Kautschuk* **6**, 234 (1930).
[52] We wish to express our appreciation to Dr. van Harpen, Medan, Sumatra, for his kindness in furnishing us with a large quantity of gutta-percha latex, and to the management of the Norddeutschen Kabelwerke, Nordenham, for furnishing a similar quantity of balata latex, both having been tapped from virgin trees.
[53] Branching also is brought about in rubber by autoöxidation (see page 493).
[54] Staudinger and Bondy, *Ann.* **468**, 1 (1929); Fischer, "Gutta-Percha and Balata", Allgem. Industrieverlag, Berlin, **1933**, p. 84.
[55] Gutta-percha and balata are much more easily prepared in pure form than is rubber.
[56] All the elementary analyses described in this work were carried out by S. Kautz in the laboratory of microchemistry of the Research Department of Macromolecular Chemistry.
[57] Schulz, *Z. physik. Chem.* **176A**, 317 (1936).
[58] We wish to express our appreciation to the management of the firm of Krupp A.-G., Essen, for supplying us with this steel. For the use of V-4-A steel osmometers in osmotic measurements, see Staudinger and Schulz, *Ber.* **70**, 1577 (1937).
[59] With respect to the difficulties involved in these viscosity measurements, and the tendency toward degradation from traces of oxygen, which are manifest by changes in viscosity, see Staudinger and Leupold, *Ber.* **63**, 730 (1930).
[60] Staudinger and Heuer, *Z. physik. Chem.* **171A**, 129 (1934).
[61] Staudinger and Staiger, *Ber.* **68**, 718 (1935).
[62] Staudinger and Staiger, *Ber.* **68**, 707 (1935).
[63] Pummerer and Pahl, *Ber.* **60**, 2152 (1927).

[64] Pummerer and his coworkers designate these ether-soluble portions as "ether sol rubber", and distinguish them from "ether gel rubber". They remark that gel formation is to be regarded as an orientation phenomenon of colloidchemical or even crystallographic nature, brought about by extramolecular forces, and therefore is to be regarded as probably an association rather than as a form of polymerization through primary valences (see Pummerer, Gündel and Andriessen, *Ber.* **61**, 1590 (1928)). On the contrary, the present authors have proved that rubber is composed of a mixture of homologous polymers, and that the ether-soluble portions have lower average degrees of polymerization than the ether-in-soluble, benzene-soluble portions (see Staudinger and Bondy, *Ann.* **488**, 153 (1931)). In the transformation of soluble rubber into insoluble rubber, a network of fibre molecules is formed through the agency of oxygen. The higher the molecular weight of a rubber, the smaller the proportion of oxygen necessary to bring about this network formation. Therefore this network is formed much more readily in the benzene-soluble component of rubber than in the low-molecular, ether-soluble component. In this way it is possible to explain the observations of Pummerer and his coworkers. In this connection, the similar relations existing in the mixed polymers of styrene and divinylbenzene should be noted. The higher the average degree of polymerization of polystyrene, the smaller the proportion of divinylbenzene necessary to transform soluble polystyrene of unlimited swelling power into an insouble product of limited swelling power (cf. Staudinger and Husemann, *Ber.* **68**, 1618 (1935)). With respect to the separation of rubber into homologous polymers, see Staudinger and Bondy, *Ann.* **488**, 153 (1931).

[65] Staudinger and Bondy, *Ann.* **488**, 153 (1931).

[66] Winterstein and Stein, *Z. physiol. Chem.* **220**, 247 (1933).

[67] The rubber latex was furnished by the Metallgesellschaft, Frankfurt am Main, through the kindness of Dr. Schweizer.

[68] The ease with which the purified rubber became so extraordinarily insoluble is surprising, in view of the fact that at no time during the investigation was a transformation of gutta-percha into an insoluble form observed. At the moment, there is no explanation of these differences between the two polyprenes.

[69] Dogadkin and Lawrenenko, *Kautschuk* **9**, 97 (933). For different observations, see Haller, *Kolloid-Z.* **56**, 257 (1931).

[70] The crude rubber examined by Caspari probably contained antioxidants and was therefore relatively insensitive. Accordingly the measurements should be repeated with crude rubber from fresh latex.

[71] This technical product was obtained through the kindness of the I. G. Farben-industrie, Ludwigshafen.

[72] Harries, *Ber.* **37**, 2708 (1904); "Untersuchungen über die Natürlichen and Kunstlichen Kautschuke", Springer, Berlin, **1919**, p. 50.

[73] The filtrate contained manganese dioxide in colloidal solution. This cannot be removed by sulfur dioxide because the latter reacts with rubber and converts it into insoluble transformation products.

[74] Bruson, Sebrell and Calvert, *Ind. Eng. Chem.* **19**, 1033 (1927)).

[75] Staudinger and Widmer, *Helv. Chim. Acta* **9**, 529 (1926); Staudinger, "Die Hochmolekularen Organischen Verbindungen: Kautschuk und Cellulose", Springer Berlin, **1932**, p. 38*b*.

[76] Staudinger, *Chem.-Ztg.* **58**, 225 (1934); *Kautschuk* **5**, 126 (1929); Staudinger and Bondy, *Ann.* **488**, 138 (1931).

[77] Staudinger, Swiss patent 119, 027; Busse, *Ind. Eng. Chem.* **24**, 140 (1932); Grenquist, *Ind. Eng. Chem.* **22**, 759 (1930).

[78] Mojen, *Kautschuk* **13**, 39 (1937).

[79] Staudinger and Widmer, *Helv. Chim. Acta* **9**, 529 (1926).

[80] With respect to the admissibility of this method, see Staudinger and Rheiner, *Helv. Chim. Acta* **7**, 23 (1924); Staudinger, *Ber.* **57**, 1203 (1924); *Kolloid-Z.* **54**, 129 (1931); Staudinger and coworkers, *Helv. Chim. Acta* **13**, 1334 (1930); Schmidt, *Z. physik. Chem.* **159A**, 337 (1932).

[81] Staudinger and Bondy, *Ann.* **468**, 1 (1929).

[82] The observation that these polypranes, unlike polyprenes, give stable solutions led earlier to the proof that the instability of solutions of polyprenes, including rubber, is to be ascribed, not to a micellar structure, but to the extreme sensitivity of the micromolecules because of their double bonds. See Staudinger, *Helv. Chim. Acta* **13**, 1324 (1930); Staudinger, Geiger, Huber, Schaal and Schwalbach, *Helv. Chim. Acta* **13**, 1334 (1930).

[83] If it is desired to transform a polyprene into its corresponding polyprane, it should be treated in very dilute solution with a large excess of the catalyst. See Staudinger and Leupold, *Ber.* **67**, 304 (1934).

[84] Staudinger, German patent 415,871; Staudinger and Fritschi, *Helv. Chim. Act* **5**, 785 (1922); Staudinger, *Ber.* **57**, 1203 (1930).

[85] For the use of decalin in the reduction to hydrorubber, see E. I. du Pont de Nemours & Co., British patent 443,883.

[86] Raney, U. S. patent 1,628,190; Covert and Adkins, *J. Am. Chem. Soc.* **54**, 4116 (1932).

[87] The authors wish to show their appreciation to the management of the Deutsche Nickelwerke, Schwerte (Ruhr) for placing at their disposal large quantities of this alloy.

[88] This autoclave is manufactured by the firm of Andreas Hofer, Mülheim(Ruhr).

[89] Staudinger and Leupold, "Die Hochmolekularen Organischen Verbindungen: Kautschuk und Cellulose", Springer, Berlin, **1932**, p. 440.

[90] Calculated by difference.

[91] The authors wish to express their appreciation to the management of the I. G. Farbenindustrie, Ludwigshafen, for their kindness in furnishing this hydrorubber.

[92] Staudinger and Mojen, *Kautschuk* **12**, 159(1936).

[93] Such a change in form of the molecules by cyclization is not excluded *a priori*. In the first experiments on hydrogenation, which were carried out by Pummerer, it is probable that the rubber was not hydrogenated but was cyclized. See Pummerer and Burkhard, *Ber.* **55**, 3458 (1922); Staudinger, *Ber.* **57**, 1203 (1924).

[94] Staudinger and Nodzu, *Helv. Chem. Acta* **13**, 1350 (1930).

[95] Staudinger and Mojen, *Kautschuk* **12**, 121 (1936).

[96] Staudinger and Husemann, *Ann.* **527**, 195 (1937).

[97] Staudinger and Bondy, *Ann.* **468**, 1 (1929).

[98] Meyer and Mark assume that the macromolecules of rubber have the *cis*-form, and those of guttapercha the *trans*-form. See Meyer and Mark, "Der Aufbau der hochpolymeren organischen Naturstoffe", Akademische Verlagsgesellschaft, Leipzig, **1930**, p. 189. This view is held by Sauter also (*Z. physik. Chem.* **36B**, 405 (1937). Staudinger, on the contrary, is of the opinion that the relations are just the reverse (cf. *Ber.* **63**, 927 (1930)).

[99] Haller, *Kolloid-Z.* **49**, 74 (1929); **56**, 257 (1931); Guth and Mark, *Monatsh.* **65**, 93 (1935); *Naturwissenschaften* **25**, 353 (1937); Meyer and Ferri, *Helv. Chim. Acta* **18**, 570 (1935); Meyer, von Susich and Valkó, *Kolloid-Z.* **59**, 208 (1932).

[100] Katz, *Naturwissenschaften* **13**, 410 (1925); *Kolloid-Z.* **36**, 300 (1925).

[101] Kuhn, *Kolloid-Z.* **68**, 2 (1934); **76**, 258 (1936); *Z. angew. Chem.* **49**, 858 (1936); **51**, 640 (1938).

[102] Sauter, *Z. physik. Chem.* **36B**, 242 (1937).

[103] Park, *Ind. Eng. Chem.* **17**, 152 (1925).

[104] Staudinger and Bondy, *Ber.* **63**, 734 (1930); Staudinger, *Ber.* **63**, 921 (1930); Staudinger, *Helv. Chim. Acta* **13**, 1324 (1930); Staudinger and Leupold, *Ber.* **67**, 304 (1934); Staudinger, *Kautschuk* **10**, 157, 170, 192 (1934).

[105] Fikentscher and Mark, *Kolloid-Z.* **49**, 135 (1929).

[106] Eisenschitz, *Z. physik. Chem.* **163A**, 133 (1933); Kuhn, *Kolloid-Z.* **68**, 2 (1934).

[107] Staudinger and Schneiders, *Ann.* **541**, 151 (1939); Staudinger and Warth, *J. prakt. Chem.* **155**, 261 (1940).

[108] See literature references in Table 38.

[109] Staudinger and Schneiders, *Ann.* **541**, 151 (1939).

[110] Staudinger and Warth, *J. prakt. Chem.* [2] **155**, 261 (1939).

[111] Staudinger and Schneiders, *Ann.* **541**, 151 (1939); Staudinger and Warth, *J. prakt. Chem.* [2] **155**, 261 (1939).

[112] Kirchhof, *Kautschuk* **5**, 175 (1929).

[113] Staudinger and Staiger, *Ber.* **68**, 707 (1935); Staudinger and Schwalenstöcker, *Ber.* **68**, 727 (1935); Staudinger and Moser, *Ber.* **60**, 208 (1936).

[114] Staudinger and Schmidt, *J. prakt. Chem.* **155**, 129 (1940); Kraemer and van Natta, *J. Phys. Chem.* **36**, 3186 (1932); unpublished experiments of O. Nuss.

[115] See later work.

[116] Staudinger and Schmidt, *J. prakt. Chem.* [2] **155**, 129 (1940); unpublished experiments by O. Nuss.

[117] Pummerer, Ebermayer and Gerlach, *Ber.* **64**, 816 (1931).

[118] Possibly a more detailed investigation of the byproducts which are formed by this ozonization would give a further insight into the nature of the branching.

[119] Uupublished experiments of E. Plötze.

[120] Staudinger and Husemann, *Ann.* **527**, 195 (1937).

[121] Staudinger and Schneiders, *Ann.* **541**, 151 (1939).

[122] Staudinger and Warth, *J. prakt. Chem.* [2], **155**, 261 (1940).

[123] Staudinger and Schulz, *Ber.* **68**, 2320 (1935).

[124] Staudinger and Bondy, *Ann.* **468**, 1 (1929).

[125] This is naturally true also of the corresponding cellulose derivatives (cf. Staudinger and Schweitzer, *Ber.* **63**, 3132 (1930)). The same relations hold true of mannans (cf. Husemann, *J. prakt.* Chem. **155**, 241 (1940).

[126] Objection can be raised to the use of freezing-point depressions as a means of evaluation because they may lead to incorrect results in determining molecular weights, for abnormal freezing-point depressions have been frequently observed in recent times in various series of high-polymeric substances. See Staudinger and Dreher, *Ann.* **517**, 73 (1935); Staudinger, Kern and Herrara, *Ber.* **68**, 2346 (1935).

[127] Staudinger and Bondy, *Ann.* **468**, 1 (1929); Staudinger and Rheiner, *Helv. Chim. Acta* **7**, 23 (1924).

THE CONSTITUTION OF BUTADIENE POLYMERS

COMMUNICATION NO. 259 ON MACROMOLECULAR COMPOUNDS

COMMUNICATION NO. 50 ON RUBBER *

H. STAUDINGER and KL. FISCHER

DEPARTMENT OF RESEARCH ON MACROMOLECULAR CHEMISTRY, CHEMICAL LABORATORY, UNIVERSITY OF FREIBURG I. BR., GERMANY

BRANCHING IN THE MACROMOLECULES OF POLYBUTADIENES

When butadiene is polymerized, the resulting polymers are composed of macromolecules which have branched structures. The actual linking of butadiene molecules to form polymers may proceed in different ways[1]. Not only can linking take place at the 1,4-position (see Formula 1) or at the 1,2-position (see Formula 2), but an addition reaction can take place at the 1,2- and 1,4-positions (see Formulas 3a and 3b). As a result, extensively branched molecules are formed, for the lateral chains unite by means of their double bonds with more butadiene molecules, either in the 1,2-position or in the 1,4-position. Finally it is not impossible that, to at least a small extent, two butadiene molecules unite directly, in accordance with a diene synthesis, to form vinylcyclohexene[2], which, after activation of its double bonds, reacts with more butadiene molecules in the 1,2-position or in the 1,4-position[3].

Technically, butadiene was at first polymerized with sodium[4] (Bunas with numerical designations), but today it is polymerized chiefly in the emulsified form[5], and this process is used also to prepare mixed polymers[6] (Bunas with letter designations). In the investigation to be described, this latter group of Buna rubbers was not studied, because in most cases they are insoluble, or swell only to a limited extent, and therefore it is impossible to determine either the size or the shape of their macromolecules, as can be done with soluble sodium polymers and emulsion polymers.

An insight into the constitution of polybutadiene is gained by studying its ozone cleavage. In this case, only very small yields (approximately 20 per cent) of succinic acid or succinic aldehyde[7] are formed, whereas these latter would be the chief reaction products if polybutadiene has the constitution shown in formula (1). Furthermore, ozone cleavage does not give any pure highly-polymeric polyacrylic acid or aldehyde, which would be expected from a polybutadiene of the constitution shown in formula (2)[8]. Instead, a mixture of lower and higher molecular cleavage products is formed, possibly from addition products corresponding to formulas (3a) and (3b).

In more recent investigations, butane-1,2,4-tricarboxylic acid was found among the products of ozone cleavage[9]. This is certain proof of branching in the molecules of polybutadiene, since an acid of this character could be formed only from a polymerization product of the formula (3a). That a butadiene molecule adds to other reactive molecules, not only in the 1,4-position but also in the 1,2-position, is proved by the addition of butyl lithium to butadiene[10].

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Journal für Praktische Chemie*, Vol. 157, Nos. 4-7, pages 158-176, January 23, 1941. For the 258th Communication on Macromolecular Compounds, which is also the 49th Communication on Isoprene and Rubber, see Staudinger and Fischer, *Journal für Praktische Chemie*, Vol. 157, Nos. 1-3, pages 19-88, December 24, 1940; RUBBER CHEMISTRY AND TECHNOLOGY, preceding article.

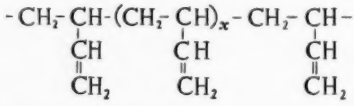
It had previously been concluded that macromolecules of polybutadiene have a complicated structure, because the hydrogenation product of butadiene is not a normal high-molecular paraffinic hydrocarbon[11], whereas a hydrocarbon of this latter type would be formed by hydrogenation if polybutadiene has the structure represented by formula (1). Furthermore an unbranched high-molecular paraffin hydrocarbon is very difficulty soluble in organic solvents, and crystallizes well[12]. On the contrary, hydropolybutadiene is similar in appearance to hydrorubber, *i.e.*, is an amorphous mass which dissolves with relatively ease in organic solvents. A high-molecular paraffin hydrocarbon is readily soluble if it contains side chains[13], but these side chains are retained in its reduction product only if the starting material itself is composed of branched macromolecules.

Formula 1 (1,4-addition)

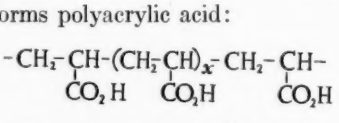
$$-CH_2-CH=CH-CH_2-(CH_2-CH=CH-CH_2)_x-CH_2-CH=CH-CH_2-$$

When ozonized, this forms succinic dialdehyde, $O=CH-CH_2-CH_2-CH=O$ or succinic acid, $HO_2C-CH_2-CH_2-CO_2H$.

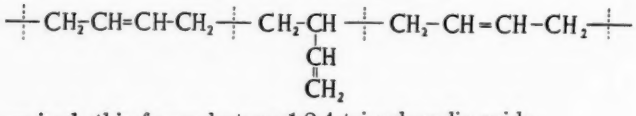
Formula 2 (1,2-addition)



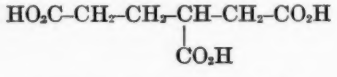
When ozonized, this forms polyacrylic acid:



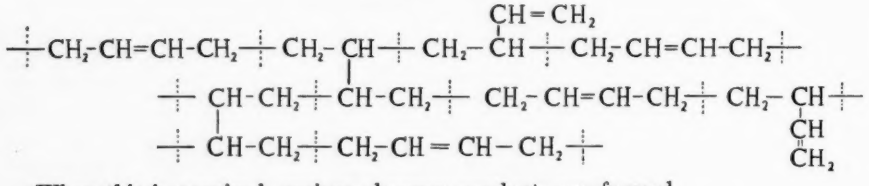
Formula 3a (1,2-1,4-addition)



When ozonized, this forms butane-1,2,4-tricarboxylic acid:



Formula 3b (1,2-1,4-addition)



When this is ozonized, various cleavage products are formed.

Several technical grades of polybutadiene were investigated. Their molecular weights were determined by the osmotic method, and their K_m and $K_{equiv.}$ values were calculated from viscosity measurements. It was assumed that these polybutadienes would be certain to have low K_m and $K_{equiv.}$ values because of branchings in their molecules; in fact, it was expected that these values would be lower

than those of rubber itself, because in the case of branched molecules, the number of primary molecules which compose the main chains, relative to the total number of primary molecules from which the macromolecules are formed, is smaller than in the case of unbranched fibre molecules, in which all the primary molecules function as component parts of the chains.

PURIFICATION OF THE PRODUCTS

A sodium polymer (B-85) and two emulsion polymers which were obtained from a technical source were investigated[14]. One of these latter was prepared with a high proportion of controlling agent, the other with a small proportion of the same agent. All three of these Buna products were soluble in organic solvents. On the contrary, because of the extensive network formation of their fibre molecules, mixed polymers with styrene and acrylonitrile (numbered Bunas) are not soluble products with unlimited swelling, but are more or less insoluble products which swell only to a limited extent. Furthermore it should not be forgotten that soluble types of Buna become insoluble very rapidly when allowed to stand in air and light because, as with rubber, a reciprocal network formation of the fibre molecules takes place. As a result, a system of soluble colloidal molecules with unlimited swelling capacity are transformed into an insoluble product of limited swelling capacity[15].

This transformation frequently takes place within a few days, and products which have been purified by repeated precipitation are more sensitive in this respect than the corresponding crude technical products, because anticatalysts, *e.g.*, phenyl-β-naphthylamine, which prevent oxidation, are removed in the process of purification. Also solutions of Buna change very readily in air and light, and it has been frequently observed that the viscosities of such solutions increase as a result of the tendency of the macromolecules to form chains.

In purifying the technical butadiene polymers, they were first extracted with acetone for 1-2 days; the hydrocarbons were then dissolved in toluene, and the insoluble components were removed from the solutions by filtering through cotton filters. To facilitate this filtration, the viscosities of the toluene solutions were reduced by adding a small proportion of acetone. By this means, swelling of the insoluble substances was reduced somewhat, and they could be filtered off more easily. Finally the solutions were filtered through a Soxhlet filter and through very porous paper. The butadiene polymers were precipitated from their solutions by adding methanol, and were again dissolved in toluene. From these toluene solutions, separate fractions were precipitated by adding methanol gradually. As a rule the first of these fractions was discarded, since it contained impurities. The individual fractions were then purified by repeated precipitations. The purified butadiene polymers obtained in this way were stored in the form of solutions because, in the solid state, the products became insoluble very quickly. The percentages of solids in the solutions were determined by evaporation.

As in investigations on rubber and gutta-percha, it was necessary to carry out all the operations which have just been described with the most rigorous exclusion of air. To this end, vessels of brown glass were used so as to avoid polymerization by the action of light. In all the osmotic and viscosity measurements to be described, the same precautions were taken in following through the procedures[16].

That the polybutadienes were almost pure is evident by the analyses shown in Table I.

OSMOTIC MEASUREMENTS

The osmotic measurements were carried out, as they were with rubber, in toluene in osmometer cells constructed of V-4-A steel[17], with exclusion of air and

TABLE I

ANALYSIS OF BUTADIENE POLYMERS

Product	Degree of polymerization	Carbon (percentage)	Hydrogen (percentage)	Ash (percentage calculated by subtraction)
Sodium polymer B-85				
Easily soluble fraction	1,450	88.69	11.28	Free
Difficultly soluble fraction	2,400	88.50	11.16	Free
Emulsion polymer with much controlling agent				
Easily soluble fraction	1,000	88.73	11.34	Free
Middle fraction	1,400	87.20	11.58	Free
Difficultly soluble fraction	2,100	87.61	11.06	0.28
Emulsion polymer with little controlling agent				
Easily soluble fraction	4,300	88.48	11.43	Free
Difficultly soluble fraction	8,200	88.86	11.29	Free
Calculated for $(C_4H_6)_x$	—	88.81	11.19	—

light; and only those experiments in which the viscosities of the solutions remained practically unchanged before and after the measurements[18] were considered to be reliable.

The limiting values of p/c as c approached zero were determined by graphical extrapolation from the p/c values at different concentrations.

The molecular weights derived from the limiting p/c values as c approached zero were used in calculating the s values by the formula of Schulz[19]. The s values of the various polymers do not fall on a straight line; this is evidence that they are not homologous polymers. The s values of the emulsion polymers prepared with a high proportion of controlling agent lie on a straight line which is different from that of the emulsion polymers prepared with a small proportion of controlling agent, and is different also from that of the sodium polymer. The s values of the last two fall on a straight line.

Table III gives a summary of the average degrees of polymerization of the butadiene polymers calculated from the limiting p/c values and also from the s values.

TABLE III

COMPARISON OF THE AVERAGE DEGREES OF POLYMERIZATION OF BUTADIENE POLYMERS CALCULATED BY THE METHODS OF LIMITS AND FROM THE s VALUES

Product	$\lim_{c\to 0} (p/c)$	Average degree of polymerization from $\lim_{c\to 0} (p/c)$	Average degree of polymerization from the s values
Sodium polymer B-85			
Easily soluble fraction	0.34	1,300	1,450
Difficultly soluble fraction	0.19	2,300	2,400
Emulsion polymer with much controlling agent			
Easily soluble fraction	0.49	900	1,000
Middle fraction	0.32	1,350	1,400
Difficultly soluble fraction	0.23	1,900	2,100
Emulsion polymer with little controlling agent			
Easily soluble fraction	0.11	4,000	4,300
Difficultly soluble fraction	0.05	8,800	8,200

TABLE II

OSMOTIC MEASUREMENTS OF BUTADIENE POLYMERS IN TOLUENE

Product	Concentration c (g. per l.)	$p \times 10^3$	$(p/c) \times 10^3$	Specific active volume (s)	Average molecular weight	Average degree of polymerization
Sodium polymer B-85						
Easily soluble fraction	1.90	0.76	0.40	0.125	81,000	
	4.06	1.83	0.45	0.088	85,000	
	5.72	2.90	0.51	0.073	83,000	
	8.40	5.18	0.62	0.058	78,000	
					81,000	1,450
Difficultly soluble fraction	2.00	0.50	0.25	0.150	140,000	
	4.00	1.26	0.31	0.100	129,000	
	6.05	2.10	0.35	0.082	141,000	
	8.02	3.33	0.42	0.070	134,000	
	10.20	4.98	0.49	0.058	123,000	
					133,000	2,400
Emulsion Buna with much controlling agent						
Easily soluble fraction	2.15	1.15	0.54	0.077	55,000	
	5.80	3.78	0.65	0.049	53,000	
	7.91	5.30	0.67	0.042	55,000	
					54,000	1,000
Middle fraction	2.14	0.82	0.38	0.092	80,000	
	3.99	1.58	0.40	0.070	87,000	
	5.99	2.97	0.50	0.054	74,000	
	7.93	4.36	0.55	0.046	70,000	
					78,000	1,400
Difficultly soluble fraction	1.85	0.49	0.27	0.106	115,000	
	3.70	1.08	0.29	0.082	121,000	
	4.60	1.53	0.33	0.074	112,000	
					116,000	2,100
Emulsion Buna with little controlling agent						
Easily soluble fraction	2.07	0.34	0.16	0.169	230,000	
	3.95	0.80	0.20	0.120	230,000	
	6.24	1.64	0.26	0.092	217,000	
	8.30	2.47	0.30	0.077	230,000	
					227,000	4,300
Difficultly soluble fraction	1.90	0.17	0.09	0.230	490,000	
	3.10	0.35	0.11	0.175	450,000	
	4.00	0.53	0.13	0.145	440,000	
	6.05	1.10	0.18	0.110	400,000	
	8.30	1.90	0.23	0.080	430,000	
					440,000	8,200

DETERMINATION OF THE K_m AND $K_{equiv.}$ VALUES OF BUTADIENE POLYMERS

The specific viscosities of the different butadiene polymers were determined in toluene at 20° C in the range of sol solutions, with exclusion of air and light and, in the determination of each η_{sp}/c value, and of each viscosity value as well, at least two weighings were made (see Table IV).

The temperature relation, *e.g.*, the relation of the η_{sp}/c values at 60° C to those at 20° C is approximately 0.95 and is, therefore, the same as that of rubber solutions and gutta-percha solutions[20] (see Table V).

TABLE IV

VISCOSITY MEASUREMENTS OF SOLUTIONS OF BUTADIENE POLYMERS IN TOLUENE AT 20° C

Product	Concentration	η_r	η_{sp}/c
Sodium polymer B-85			
Easily soluble fraction	0.452	1.066	0.146
	0.512	0.073	0.142
Difficultly soluble fraction	0.528	1.174	0.330
	0.536	0.176	0.329
Emulsion polymer with much controlling agent			
Easily soluble fraction	0.988	1.160	0.162
	0.783	1.124	0.159
Medium fraction	0.720	1.158	0.220
	0.700	1.155	0.221
Difficultly soluble fraction	0.450	1.131	0.291
	0.520	1.147	0.283
Emulsion polymer with little controlling agent			
Easily soluble fraction	0.642	1.233	0.363
	0.660	1.235	0.357
Difficultly soluble fraction	0.414	1.232	0.561
	0.418	1.237	0.567

TABLE V

COMPARISON OF THE η_{sp}/c VALUES OF SOLUTIONS OF BUTADIENE POLYMERS AT 20° C AND AT 60° C

Product	η_{sp}/c at 20° C	η_{sp}/c at 60° C	$\frac{\eta_{sp}/c \text{ at } 60° \text{ C}}{\eta_{sp}/c \text{ at } 20° \text{ C}}$
Sodium polymer B-85			
Easily soluble fraction	0.146	0.139	0.95
	0.142	0.133	0.94
Difficultly soluble fraction	0.330	0.318	0.96
	0.329	0.310	0.94
Emulsion polymer with much controlling agent			
Easily soluble fraction	0.162	0.158	0.98
	0.159	0.149	0.94
Medium fraction	0.220	0.204	0.93
	0.221	0.209	0.95
Difficultly soluble fraction	0.291	0.269	0.93
	0.283	0.266	0.94
Emulsion polymer with little controlling agent			
Easily soluble fraction	0.363	0.346	0.95
	0.357	0.340	0.95
Difficultly soluble fraction	0.561	0.524	0.93
	0.582	0.530	0.91

Here too the K_m values were calculated from viscosity measurements and the $K_{equiv.}$ values by the osmotic method (see columns 5 and 6 of Table VI). As with rubber and gutta-percha, the K_m values and $K_{equiv.}$ values are about $\frac{1}{3}$ to $\frac{1}{5}$ those obtained from viscosity measurements of low-molecular compounds with fibre molecules[21].

TABLE VI

DETERMINATION OF THE K_m AND $K_{equiv.}$ CONSTANTS OF TOLUENE AND OF THE EXTENT OF BRANCHING OF BUTADIENE POLYMERS

Product	Degree of polymerization (osmotic)	Number of chain members	η_{sp}/c	$K_m \times 10^4$	$K_{equiv.} \times 10^4$	Apparent degree of polymerization $K_m = 3.8 \times 10^{-4}$ for benzene	Degree of polymerization (osmotic) divided by degree of polymerization (viscometric)
Sodium polymer B-85							
Easily soluble fraction	1450	5800	0.144	1.0	0.25	400	3.5
Difficultly soluble fraction	2400	9600	0.330	1.4	0.34	850	2.8
Emulsion polymer with much controlling agent							
Easily soluble fraction	1000	4000	0.161	1.6	0.40	400	2.5
Middle fraction	1400	5600	0.220	1.6	0.39	600	2.3
Difficultly soluble fraction	2100	8400	0.287	1.4	0.34	750	2.8
Emulsion polymer with little controlling agent							
Easily soluble fraction	4300	17,200	0.360	0.8	0.21	950	4.5
Difficultly soluble pattern	8200	32,800	0.571	0.7	0.17	1500	5.5
Gutta-percha	1550	6,200	0.210	1.4	0.34	550	2.8
Rubber (ether-soluble; alkali-treated by the Pummerer method)	1600	6,400	0.126	0.8	0.20	350	4.6
Rubber (treated with aluminum oxide)	5100	20,400	0.900	1.7	0.44	2400	2.1
Chlorinated rubber [25]	2600	10,400	0.077	0.30	0.074	142 [26]	18.

THE STRUCTURE OF MACROMOLECULES OF BUTADIENE POLYMERS AND OF RUBBER

If the average degrees of polymerization of the butadiene polymers are calculated from their viscosity values by means of the constant 3.8×10^{-4}, obtained from low-molecular substances with fibre molecules[22], the values thus obtained are only $\frac{1}{3}$ to $\frac{1}{5}$ of the true average degrees of polymerization derived from osmotic measurements (see Table VI). In this case also, as with rubber[23] and synthetic high polymers[24], the viscosity measurements give much too low values for the average molecular weights.

The failure of the viscometric method in the determination of the molecular weights of butadiene polymers is readily understandable, for in these products there are no simple fibre molecules but only branched elongated macromolecules. If it is assumed that the viscosity law of fibre molecules, which has been proved to hold true up to a value of 1600 chain members in the case of polyesters[27], is valid also for eucolloidal substances with a value of chain members of 10,000, it is possible to calculate from viscosity measurements the chain length and, therefore, the number of butadiene residues, which are defined by the length of these macromolecules.

The really surprising result of the present investigation is the fact that the K_m values of the butadiene polymers are approximately the same as the K_m value of rubber. It had in the beginning been assumed that these values would necessarily be lower, since, judged by chemical investigations, butadiene polymers are composed of extensively branched macromolecules.

In the case of rubber, such branching has not yet been proved conclusively by chemical investigations[28]. On the contrary, ozone decomposition indicates that at least 90 per cent of the isoprene residues in the macromolecules of natural rubber are located in the 1,4-position[29]. Since the K_m values of butadiene polymers are of approximately the same magnitude as the K_m values of rubber and of gutta-percha, one is led to the conclusion that the extent of branching of the fibre molecules of synthetic and natural hydrocarbons is approximately the same in all cases[30]. This is, in turn, an indirect proof that macromolecules of rubber and of gutta-percha are not fibre molecules after all, but that their structure is a branched one.

Naturally the branchings of the molecules of synthetic polymers and of natural polyprenes are necessarily different in character. Molecules of butadiene polymers contain numerous points of branching with relatively short side chains and relatively short chain residues, in which butadiene residues are located in the 1,4-positions, in accordance with the structure shown in formula (1), for the yields of succinic acid and the corresponding aldehyde amount to only about 20 per cent[31]. On the contrary, based on the results of ozone decomposition, rubber and gutta-percha contain most of their isoprene residues in the 1,4-position, since 90 per cent of the cleavage products correspond to this structure. Accordingly, branching in the macromolecules of natural polyprenes is rarely to be found, and therefore the lateral chains must be much longer than those in the molecules of synthetic polymers. This assumption is unavoidable, for the ratio of the total number of primary molecules of which the macromolecules are composed to those which make up the main chains is approximately the same for rubber and gutta-percha as for butadiene polymers.

As will be shown in a forthcoming work, natural gutta-percha is a homogeneous substance, and it is possible that this is true also of natural rubber. The macromolecules of such homogeneous substances are not only of the same size, but probably have similar structures. It should be possible, therefore, to represent

the structure of these substances by quite definite constitutional formulas, whereas this is not possible of synthetic butadiene polymers, because probably no two of their very irregularly formed macromolecules have the same structure.

If, in the following discussion, formulas are suggested in a tentative way to support this conclusion, it must be understood that these have a different meaning with respect to natural polyprenes than they do with respect to synthetic butadiene polymers. In the latter case, the formula represents only one of the many possible structures of the variously constructed macromolecules of these synthetic products, and it will never be possible to characterize a substance of this kind by a single structural formula. On the other hand, in the case of natural polyprenes, schematic formulas give only an incomplete picture of their constitutional formulas, and the latter can be established only by continued investigation. On the account, a completely satisfactory explanation of these homogeneous polyprenes, based on the size of their macromolecules, is still far from attainment.

It is certainly possible that rubber and gutta-percha contain branched molecules and, therefore, they possibly resemble starch more closely than they do cellulose, since natural polyprenes are substances without definite structure. If, in future investigations, it should be proved conclusively that rubber has branched macromolecules as do those of polybutadienes, and that these hydrocarbons differ only in the character of the branching, it might turn out to be very difficult to prepare polybutadienes which have as extensive a branched structure as that of rubber[32]. The general structure of rubber is, naturally, fundamentally the same as that of polybutadiene. Both substances consist of elongated macromolecules, therefore belong to the class of linear colloids, and show colloidal properties similar to the latter.

The conclusion that natural polyprene and butadiene polymers which have equal degrees of polymerization also have chains of equal lengths because their K_m values are of the same magnitude has been confirmed by other investigators. It has, for example, been shown by Philipoff[34] that deviations from the Hagen-Poiseuille law shown by solutions of natural rubbers are of approximately the same order of magnitude as the deviations shown by solutions of butadiene polymers. Since the deviations from the Hagen-Poiseuille law shown by solutions of macromolecular substances apply only to linear macromolecular compounds, and since, furthermore, these deviations increase in an homologous polymeric series with increase in the length of the chains[35], it may be concluded from the observations of Philipoff also that the lengths of the chains of the macromolecules of natural polyprenes are approximately the same as those of synthetic types of Buna[36].

In addition to this, according to the investigations of Philipoff, the increase in the η_{sp}/c values of butadiene polymers with increase in concentration within the gel range is the same as that shown by natural rubbers. As has been proved in numerous cases[37], the η_{sp}/c values of an homologous polymeric series of linear macromolecular substances in gel solution increase rapidly with increase in the concentration and in the degree of polymerization. This is to be attributed to a mutual obstruction of the fibre molecules with increase in the length of their chains.

The fact that the increases in the η_{sp}/c values of natural rubber and of butadiene polymers are approximately the same supports the view that these products have chains of approximately the same lengths. Finally solutions of synthetic butadiene polymers show approximately the same temperature-viscosity relations as those of natural polyprenes[38]. At first it seemed rather surprising that the viscosity relations of solutions of synthetic butadiene polymers were in all respects so nearly the same as those of solutions of natural rubber and of gutta-

percha, because it had been assumed that butadiene polymers contain extensively branched macromolecules, whereas the macromolecules of rubber and of gutta-percha were supposed to be unbranched. Now that it has been proved in these investigations that the K_m values of synthetic and natural rubber hydrocarbons are approximately the same, the corresponding viscosity relations become readily understandable. Here too, a comparison of the viscosity relations leads to the conclusion that the fibre molecules of rubber and of gutta-percha must be branched, like those of butadiene polymers, even if the presence of branching in natural hydrocarbons has not yet been proved by chemical means.

The individual butadiene polymers do not in all cases show the same K_m values. Rather emulsion polymers which are prepared with a small proportion of controlling agent give K_m values approximately one-half those of emulsion polymers prepared with a high proportion of controlling agent. From this it may be concluded that the products prepared with a small proportion of controlling agent have more extensive branching than those of products prepared with a high proportion of controlling agent. It is probable that the physical properties of both these types of polymers, *e.g.*, their elasticity, are different because of the different structures of their molecules. To obtain a better insight into the relations between molecular branching and physical properties, products of the same average degrees of polymerization, as determined osmotically, but branched to different extents, and therefore having different K_m values, must be investigated. With this in view, butadiene polymers prepared under the most widely different conditions possible should be studied thoroughly.

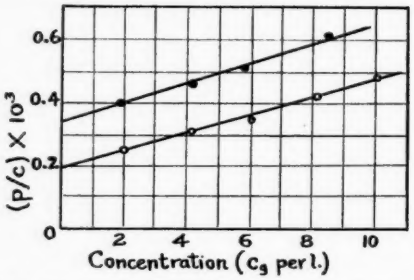


FIG. 1.—(p/c)-c Curves of sodium butadiene polymer B-85 in toluene at 27° C.
● Easily soluble fraction
○ Difficultly soluble fraction

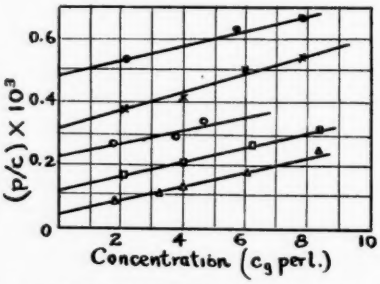


FIG. 2.—(p/c)-c Curves of emulsion polymers prepared with small and large proportions of controlling agent in toluene at 27° C.
Emulsion polymer with large proportion of controlling agent
● Easily soluble fraction
× Middle fraction
○ Difficultly soluble fraction
Emulsion polymer with small proportion of controlling agent
□ Easily soluble fraction
Δ Difficultly soluble fraction

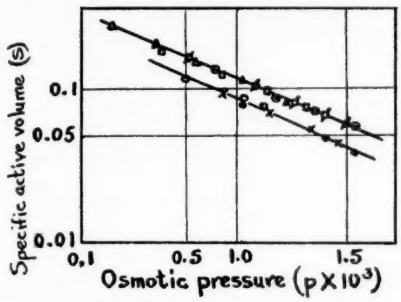


FIG. 3.—Relation between specific active volume (s) and osmotic pressure (p) of sodium-butadiene polymer B-85 and of emulsion polymers, prepared with small and large proportions of controlling agent, in toluene at 27° C.

Sodium polymer B-85.

Easily soluble fraction
Difficultly soluble fraction

Emulsion polymer with large proportion of controlling agent

Easily soluble fraction
Middle fraction
Difficultly soluble fraction

Emulsion polymer with small proportion of controlling agent

Easily soluble fraction
Difficultly soluble fraction

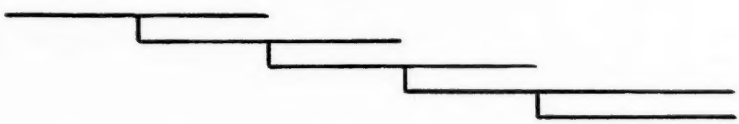


FIG. 4(A).—Schematic representation of a macromolecule of gutta-percha.

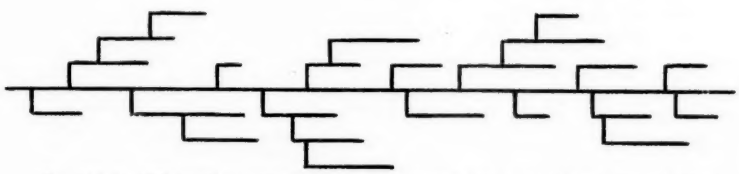


FIG. 4(B).—Schematic representation of a macromolecule of a butadiene polymer.

ACKNOWLEDGMENT

The work described in the present paper was supported by the Deutsche Forschungsgemeinschaft, whose aid the authors appreciate deeply. Likewise the authors wish to show their appreciation of the aid given by the Förderungsgemeinschaft der Forschungsabteilung für Macromolekulare Chemie.

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VISCOSITY MEASUREMENTS OF LOW-MOLECULAR COMPOUNDS IN BENZENE AT 20° C

Compound	No. of chain members	η_{sp}/c (experimental)	η_{sp}/c (calculated) $K_{equiv.} = 0.95 \times 10^{-4}$
Dimethyl diacetylmalonate	33	0.0034	0.0031
Methyl diacetylacetate	33	0.0033	0.0031

[31] Hill, Lewis and Simonsen, *Trans. Faraday Soc.* **35**, 1067 (1939).
[32] It is possible that the differences in certain of the physical properties of rubber and of polybutadiene is attributable to differences in the branching of the chains.
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[36] We have calculated the average degree of polymerization of a Buna-115 product from viscosity measurements in tetrachlorethane carried out by Philipoff (cf. *Kautschuk* **13**, 149 (1937). Based on a K_m value of 1.4×10^{-4}, this average value is 1850, *i.e.*, approximately the same as the average degrees of polymerization of the products investigated in the present work.

VISCOSITY MEASUREMENTS IN TETRACHLORETHANE AT 19.8° C CARRIED OUT BY PHILIPOFF

Concentration c (g. per l.)		η_{sp}/c	Average degree of polymerization
0.025	1.062	0.250	
0.050	1.150	0.300	
0.100	1.240	0.250	
	Average	0.260	1850

It must be taken into account that Buna is degraded to a considerable extent in tetrachlorethane, because the latter evolves hydrogen chloride easily, and polyprenes undergo autoöxidation, extraordinarily easily in acid solutions (cf. Staudinger and Mojen, *Kautschuk* **13**, 39 (1937)).
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[38] Staudinger and Fischer, *J. prakt. Chem.* [2] **157**, 19 (1940). Compare Tables 16 and 22 with Table 5 of the present work.

THE MOLECULAR WEIGHTS OF RUBBER AND RELATED MATERIALS

III. A CORRECTION OF PART II *

G. GEE

THE BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION, WELWYN GARDEN CITY, HERTFORDSHIRE, ENGLAND

In the previous paper of this series[1], data on the viscosity and osmotic molecular weights of a series of rubbers were presented. The basis of the viscosity values was Lansing and Kraemer's comparison[2] of the viscosity of a sample of sol rubber in ether with its ultra-centrifuge molecular weight. An unfortunate error was made in interpreting their data, by reading their definition of intrinsic viscosity as $\lim_{c\to 0} \frac{\log_{10} \eta r}{c}$ instead of $\lim_{c\to 0} \frac{\log_e \eta r}{c}$. As a result, the argument must now be revised, as follows.

The comparison between the intrinsic viscosity $[\eta]$ and molecular weight of a high-molecular substance should either be made on homogeneous material or, alternatively, the weight average molecular weight should be used. No strictly monodisperse rubber has been prepared, but Bloomfield and Farmer[3] have separated rubber into a series of very closely defined fractions. From their method of isolation, these are believed to be reasonably homogeneous and, in any case, a considerable degree of inhomogeneity is required to make the weight and number average molecular weights seriously different[4]. Hence it is legitimate to compare the osmotic molecular weights of these fractions with their intrinsic viscosities. This is done in Table I, and it will be noted that the ratio of M_{osmotic} to $[\eta]$, in benzene + 15% methanol, is constant within experimental error.

TABLE I

Fraction	$10^{-5} M_{\text{osmotic}}$	$[\eta]$ in benzene + 15% methanol	$10^{-4} \frac{M}{[\eta]}$
Hydrocarbon from oxide fraction.....	0.66 ± 0.03	0.61_5	10.7
Low latex fraction.....	2.1 ± 0.3	2.3_5	9.0
Intermediate latex fraction.....	3.5 ± 0.2	3.5	10.0

The middle value is the least certain, and a weighted mean of 10.2 is taken for the ratio. The conclusion to be drawn from these results is that Staudinger's law holds over the molecular-weight range of 60,000 to 350,000. To apply the law to other solvents, it is necessary only to compare the intrinsic viscosities of any rubber in a range of solvents, since it has been shown in Table V[1] that the ratio of the intrinsic viscosities of a substance in two solvents is independent of the molecular weight of the material. Starting from the above constant for benzene + 15% methanol and proceeding in this way, we can arrive at the list of Staudinger constants given in Table VI[1].

Lansing and Kraemer's ultracentrifuge and viscosity data provide an independent basis for the derivation of the Staudinger constant for ether, although

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they do not in themselves make it possible to test the validity of Staudinger's law. Their constant for ether is 21.6×10^4, which is to be compared with our value of 9.4×10^4. This discrepancy cannot be resolved by assuming the fractions to be highly polydisperse and it is, therefore, necessary to choose between the two possible bases for viscosity-molecular weight calculations. The osmotic data are preferred, both on account of the more direct nature of the comparison involved, and because of the paucity of ultracentrifuge data for rubber or, indeed, for nonaqueous solutions in general. The constants given in Part II are, therefore, still considered to afford the best available basis for the calculation of the molecular weights of rubbers from viscosity data.

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PERMEABILITY IN RELATION TO VISCOSITY AND STRUCTURE OF RUBBER *

RICHARD M. BARRER

CHEMICAL LABORATORIES, THE TECHNICAL COLLEGE, BRADFORD, ENGLAND

With the application of a new method of interpreting permeability data[1], simple kinetic observations can be made to give:

(1) the permeability constant P of gas through rubber.
(2) the diffusion constant D of gas within the rubber substance.
(3) the solubility C of gas or vapor in the rubber substance.

The data obtained have been used to determine the influence of temperature on flow process and solubilities, respectively, and from the latter the affinity of the solute for the rubber and the heat and entropy of solution were obtained. On the information thus obtained, theories of flow and solution processes may adequately be based. Such theories have already been outlined[1], but will be placed on a quantitative basis in this paper and related to the viscosity of rubber. First, however, the permeability is briefly discussed in relation to other properties of rubber.

FEATURES OF THE PERMEATION PROCESS

Pure rubber is relatively impermeable, both to water and to simple gases[2]. Natural rubbers may, however, contain hydrophilic impurities which cause them to swell in water, and which render them more permeable to water. Synthetic rubbers do not normally show such a property, owing to their greater purity.

Fick's laws $\left(P = -D\,\frac{\partial c}{\partial x};\ \frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \right)$ are admirably obeyed when simple solutes diffuse in rubber, but the more the latter imbibes the solute, the greater are the departures from these simple expressions. Such departures have been discussed[2], and it has been established that the concentration gradients in the steady state of flow are no longer linear[3], and that solubility data are equally complex[4]. On the theoretical side, one requires for their interpretation partition functions for a system comprising a solute in a three-dimensional network which expands on imbibing the solute. For nonexpanding networks the problem is, of course, more simple.

Temperature increases both diffusion and permeation velocities exponentially, but has a much smaller effect on the solubilities of solutes, such as He, H, N and A in rubbers[1]. The values of the activation energy for diffusion differ little among themselves for simple gases, and in the equation $D = D_0\, e^{-E/(RT)}$ (E is the activation energy; D_0 is a constant), D_0 is large compared with D for most metal-metal or salt-salt diffusion systems[5]. This and the comparative

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constancy of E have led to the view that zones of disorder, which are a prerequisite to diffusion, exist in the activated state.

Small amounts of vulcanization do not appreciably modify the permeability of rubbers to simple molecules[6]. Ebonite, however, represents the limit to reaction with sulfur, and is a nonelastic solid. Permeabilities relative to rubber for He, H, and N taking H-rubber as reference system, are shown in Table I.

TABLE I

	Rubber	Ebonite
Helium	0.6	0.2
Hydrogen	1	0.025
Nitrogen	0.16	0.0001

TABLE II

Rubber	13.4
Balata	1.7
Butta-percha	2.2

Ebonite has thus become highly selective by contrast with unvulcanized or slightly vulcanized rubber[7]. This selectivity is a characteristic of rigid membranes[5] (Cellophane, silica glass, cellulose derivatives). Thus the influence of combined sulfur depends not only on the extent of vulcanization, but also on the size of the molecule being transmitted. Increasing the combined sulfur also has an effect on the sorption of organic and inorganic molecules. Benzene and water are less imbibed by cross-linked polymers than by polymers able to swell indefinitely[8].

Stereochemical factors may further modify permeability[9]. Rubber is a *cis*-isoprene polymer; balata and gutta-percha are *trans*-isoprene polymers. The relative values of hydrogen permeability are shown in Table II. This difference extends to other properties, such as density, softening point and viscosity.

ENERGY OF ACTIVATION AND ZONE OF ACTIVATION

For normal hydrocarbons, the activation energy for viscous flow, $E_{vis.}$ is initially about one-quarter of the latent heat of vaporization[10]. As the chain-length increases, the ratio becomes less than one-quarter, and E_{vis} tends to a limit of 6-8 K.cal., *i.e.*, about the energy needed to vaporize a C_6 hydrocarbon. Muller's calculations[11] show that the heat of vaporization of a single CH_2 unit

TABLE III

	ΔH^* (K. cal.)
$-O(CH_2)_{10}O\,.\,CO\,.\,(CH_2)_6CO-$	8.05
$-O(CH_2)_{10}O\,.\,CO\,.\,(CH_2)_4CO-$	8.23
$-O(CH_2)_{10}O\,.\,CO\,.\,(CH_2)_2CO$	8.55
$-O(CH_2)_2O(CH_2)_2O\,.\,CO\,.\,(CH_2)_4CO-$	8.40

is about 0.93×10^{-13} ergs, *i.e.*, 1.3 K.cal. per mol of CH_2 units; and that this is of the same order as the van der Waals potential of a CH_2 unit in the liquid. Thus E_{vis} is sufficient to loosen completely about six CH_2 units from all restraints of their neighbors. This should give a lower limit to the size of zone participating in a unit-flow process, for it is not necessary that complete detachment occur before flow takes place. The CH_2 units composing the zone of disorder need not belong to a single chain, and the length of a single flowing unit need not, therefore, be equal to the number of CH_2 groups in the zone. In rubber, $E \simeq 10{,}000$ cal., and so the lower limit to zone size should be about eight CH_2 units[12].

The heats of activation, ΔH^*, for viscous flow of some polyesters have been obtained[12], and range from 8.05 to 8.55 K.cal. (see Table III). The zone size

in the activated state should thus be very similar to those in long-chain hydrocarbons and rubber. These observations were also extended to viscous flow in sulfur by Eyring and his coworkers[13], but all the zone sizes there given appear rather large in the light of Muller's calculations.

By considering only a single term: $\left(\frac{E}{RT}\right)^{f-1}\frac{1}{(f-1)!}$, in an equation similar to Equation (8), Barrer[5] obtained $f = 13$ or 14 for the number of degrees of freedom in the activated zone for diffusion of simple solutes in rubber. Each CH_2 unit contains several degrees of freedom, some or all of which may share in the activation energy, but clearly a considerable zone of activation is once more required. This is further supported by the large entropy of activation (Table IV).

One may conclude that zones of activation will be found in numerous high-polymer systems, where diffusion or viscous flow is occurring, or in high-molecular weight liquids, especially those showing structure[14]. On the other hand, simple structureless liquids shear or interdiffuse without such zones[5], as predicted by theory.

THE FREE ENERGY AND ENTROPY OF ACTIVATION IN DIFFUSION AND VISCOUS FLOW

The motivating force, whether in chemical reaction, viscous flow or diffusion, is the free energy of activation. The viscosity, η, and diffusion constant, D, are:

$$\eta = \frac{Nh}{V} \cdot e^{\Delta G^*/(RT)} \tag{1}$$

and

$$D = \lambda^2 \frac{\kappa T}{h} \cdot e^{-\Delta G^*/(RT)} \tag{2}$$

according to the transition state method of treatment[15,16]. Here V denotes the molar volume of a flow unit, and λ is the distance moved by the diffusing particle in each unit act of diffusion. The free energy and entropy of activation for viscous flow has recently been calculated for some liquids[17], while in Table IV is given the free energy of activation for diffusion in rubbers. In Table IV also are given the entropies of activation, recalculated from data of Barrer[1, 5, 18, 19]. In both calculations, $\lambda^2 = 10^{-15}$ sq. cm. is assumed ($\lambda \simeq 3.1 \times 10^{-8}$ cm.). These large entropies of activation further emphasize the extent of the zones. By contrast, in simple liquids ΔS^* is small and often negative, unless considerable structure occurs, or the molecular weight is large[17].

SIMPLE STATISTICS OF ACTIVATED ZONES IN RUBBER

Evidence presented in this paper and elsewhere[1, 2, 5] shows that diffusion in, and viscous flow of rubber have a common background. In both cases zones of activation result in the flow phenomena. Statistics of these energy zones will now be discussed.

Suppose the assembly of hydrocarbon chains in rubber contains N_1 degrees of freedom. If an energy equal to, or greater than, E is distributed among f of these degrees of freedom, the number of such activated zones is:

$$N = N_1\left(\frac{E}{RT}\right)^{f-1}\frac{1}{f-1!}e^{-E/(RT)} \tag{3}$$

TABLE IV

FREE ENERGY AND ENTROPY OF ACTIVATION FOR DIFFUSION IN RUBBER

Diffusion system	ΔG^* at 300° K (cal. per mol.)	ΔS^* at 300° K (cal. per mol. per degree)
H-butadiene-acrylonitrile interpolymer	3540	11.40
N-butadiene-acrylonitrile interpolymer	4220	14.66
H-Neoprene	3390	12.40
A-Neoprene	3570	15.97
N-Neoprene	3320	16.67
N-butadiene methylmethacrylate interpolymer	3840	15.25
A-butadiene methylmethacrylate interpolymer	3820	13.42
N-butadiene-styrene interpolymer	6020	7.81
A-butadiene-styrene interpolymer	5240	9.26
H-chloroprene polymer	2190	15.31

Since f may have any value from unity to N_1, the total number of zones[20] is:

$$\Sigma N = N_1 e^{-E/(RT)}\left[1 + \frac{E}{RT}\frac{1}{1!} + \left(\frac{E}{RT}\right)^2 \frac{1}{2!} + \ldots + \left(\frac{E}{RT}\right)^{f-1} \frac{1}{(f-1)!} + \ldots\right] \quad (4)$$

The values of the terms in the square bracket at first increase and then decrease as f increases for $E > RT$ (Figure 1). There is thus a most probable zone size, and the most important contributions to flow occur in the zones in the region of the maxima of Figure 1. The maxima occur at values of f which increase as $E/(RT3$ increases, and the zones important for flow thus become larger at lower temperatures, or for larger E.

Diffusion in simple liquids occurs with a small activation energy (2 to 4 K.cal.). Figure 1 then predicts, as has been found[5], that the zone of disturbance in the activated state is small, one or two degrees of freedom containing all the activation energy. On the other hand, in rubbers the value of E for either viscous flow or diffusion of simple solutes is $\sim$ 10,000 cal., and at 300 K, the figure then indicates for both phenomena zones of activation where $f \sim 16$.

The considerations of this section, taken in conjunction with Equations (8) and (11), show that there should, for various systems at a constant temperature[20], be approximately linear functional relationships between E and log D_o or log η_o in the equations: $D = D_o e^{-E/(RT)}$ or $\eta = \eta_o e^{E/(RT)}$. That this is so is indicated in Figure 2, which further demonstrates continuity between liquids and rubbers as diffusion media. Such functional relationships should also exist between ΔS^* and E since, for viscous flow and diffusion, ΔS^* is a linear function of log η_o and log D_o, respectively. Thus

$$\frac{\Delta S^*}{R} = -2.303 \log \eta_o + 2.303 \log \frac{Nh}{V}$$

and

$$\frac{\Delta S^*}{R} = 2.303 \log D_o + 2.303 \log \frac{h}{\lambda^2 \kappa T} - 1$$

where D_o and η_o are defined by $D = D_o e^{-E/(RT)}$ and $\eta = \eta_o e^{E/(RT)}$, respectively. Figure 3, using data of Stearn and Eyring[17], shows the predicted relationship for viscous flow of liquids. Functional relationships have also been observed in

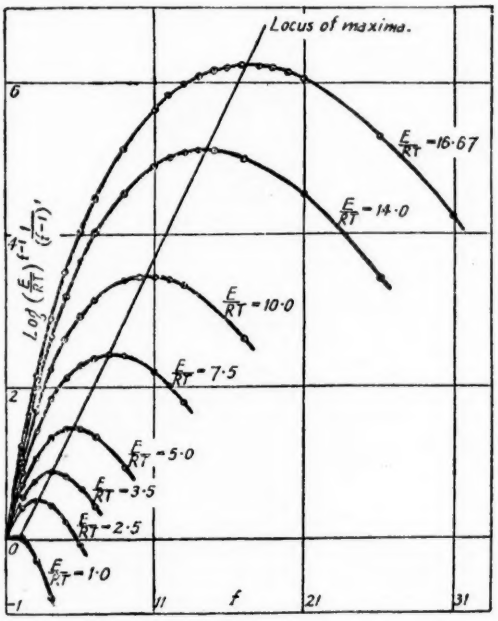

FIG. 1.—Plot of $\log\left(\frac{E}{RT}\right)^{f-1}\frac{1}{f-1!}$ in equation (2) showing maxima and locus of maxima.

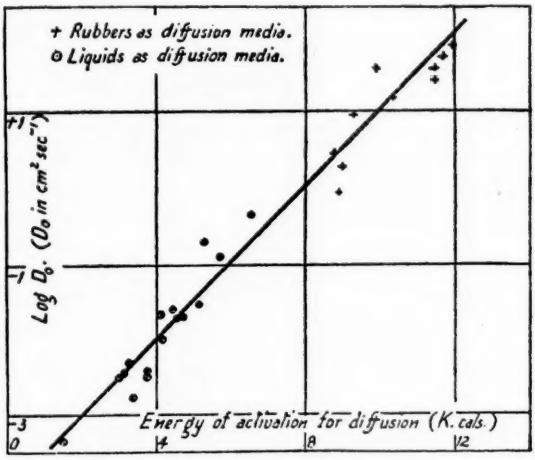

FIG. 2.—Functional relationship between log D_0 and E for diffusion. The data plotted are taken from refs. [1] and [5].

chemical kinetics[21], and emphasize the similarity between these various rate processes.

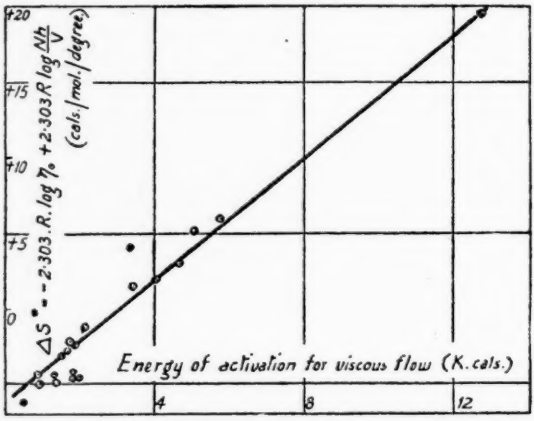

FIG. 3.—Functional relationship between ΔS^* and E for viscous flow. The data plotted are taken from ref. [15].

DIFFUSION

In a zone of disorder there are many possible sets of librations of CH_2 units, only a fraction α of which may be successful in producing net transport of a solute molecule in one direction. In the absence of external forces, α should be $\frac{1}{6}$. If the mean lifetime of the activated state is τ, and the period of a libration is τ_0, the number of successful sets of librations during the period of activation is $\frac{\alpha\tau}{\tau_0}$ per zone. The total number of sets of successful librations in zones involving the N_s solute molecules is then:

$$N_2 = N_s\, e^{-E/(RT)} \sum_{f-1}^{N_1} \frac{\tau}{\tau_0}\alpha\left(\frac{E}{RT}\right)_{f-1}\frac{1}{f-1!} \tag{5}$$

In each second, this number is

$$N_3 = N_s\, e^{-E/(RT)} \sum_{f=1}^{N_1} \frac{\alpha}{\tau_0}\left(\frac{E}{RT}\right)^{f-1}\frac{1}{f-1!} \tag{6}$$

and proceeding along lines already given[22] the value for D is:

$$D = \lambda^2\, e^{-E/(RT)} \sum_{f=1}^{N_1} \frac{\alpha}{\tau_0}\left(\frac{E}{RT}\right)^{f-1}\frac{1}{f-1!} \tag{7}$$

where λ is the average distance moved by the solute per unit act of diffusion. If the mean value of λ is 3×10^{-8} cm., $\tau_0 \sim 10^{-12}$ sec., and $\alpha = \frac{1}{6}$, then:

$$D \simeq 1.6 \times 10^{-4}\, e^{-E/(RT)} \sum_{f=1}^{N_1}\left(\frac{E}{RT}\right)^{f=1}\frac{1}{(f-1)!} \text{ sq. cm. per sec.}^{-1} \tag{8}$$

Only a few terms in the summation (*i.e.*, those at or near the maximum of Figure 1) make important contributions to D, and without serious error a single term in f will suffice, both for D and η.

VISCOSITY[23]

If F is the shearing force per unit area, the viscosity may be formally defined as $\eta = \frac{Fd}{\Delta u}$, where Δu is the relative velocity parallel to the direction of shear of two adjacent hydrocarbon chains a distance d apart. The presence of the shearing force means that more successful liberations will occur in the direction of shear than in the converse direction. If there are p CH_2 units in a zone of activation, and if each moves on an average a distance, λ_1, in a single jump, the distance moved in one second by a single CH_2 unit is $\sum \frac{Np}{N_1} \frac{\lambda_1}{\tau_0} \alpha_f$, in the direction of shear, and $\sum \frac{Np}{N_1} \frac{\lambda_1}{\tau_0} \alpha_b$ in the converse direction. The values of α in the forward and backward directions are now denoted by α_f and α_b, respectively. The net velocity of a CH_2 unit, and so the velocity imposed by shear relative to a stationary chain, is:

$$\Delta u = \sum \frac{Np}{N_1} \frac{\lambda_1}{\tau_0} (\alpha_f - \alpha_b) \tag{9}$$

Thus the viscosity is:

$$\eta = Fd \sum \frac{\tau_0 N_1}{Np\lambda_1} \frac{1}{(\alpha_f - \alpha_b)} \tag{10}$$

The ratio $\sum \frac{N}{N_1}$ may be substituted from equation (4). To a first approximation, the term $(\alpha_f - \alpha_b)$ may be given by Eyring's procedure[16] as $2\alpha \sinh \frac{bE}{2\kappa T}$, where $b \sim 10^{-22}$ cc., of the same order as the volume of a flow unit. Because $bF \ll \kappa T$ for small shearing forces, one may write $\alpha \frac{bF}{\kappa T}$ for $2\alpha \sinh \frac{bF}{2\kappa T}$, and with $d \simeq \lambda_1 \simeq 3.5 \times 10^{-8}$ cm.;

$p \simeq 10$; $\alpha = \frac{1}{6}$ and $\tau_0 \simeq 10^{-10}$ sec.:

$$\eta \simeq 6 \times 10^9 \cdot \kappa T \cdot e^{E/(RT)} \frac{1}{\sum_{f=1}^{N_1} \left(\frac{E}{RT}\right)^{(f-1)} \frac{1}{(f-1)!}} \tag{11}$$

SELF-DIFFUSION IN RUBBER

The average distance moved in one direction in one second by a single CH_2 unit is given above as $\sum \frac{Np}{N_1} \frac{\lambda_1 \alpha}{\tau_0}$. Suppose some of the CH_2 units are labelled, and that there is a concentration gradient of labelled units in the x direction. Then the procedure given by Barrer[22] leads to:

$$D_s = \frac{\lambda_1^2 \cdot \alpha}{\tau_0} \frac{Np}{N_1} \tag{12}$$

as the self-diffusion constant for the interdiffusion of the CH_2 units. Thus with $\tau_o \simeq 10^{-12}$ sec., $\lambda_1 \simeq 3.5 \times 10^{-8}$ cm., and $p \simeq 10$, one has:

$$D_s \simeq 2 \times 10^{-3}\, e^{-E/(RT)} \sum_{f=1}^{N_1} \left(\frac{E}{RT}\right)^{f-1} \frac{1}{(f-1)!} \text{ sq. cm. per sec.}^{-1} \quad (13)$$

RELATION BETWEEN D_s AND η

From (13) and (11), $D_s\eta = \kappa T$ (1.2×10^7). This product is independent of the values assigned to p, τ_o, α, and $\sum \frac{N}{N_1}$, but does depend on the values assigned to d, b, and λ_1. It may be compared with Stokes' law for diffusion in simple fluids, derived on a quite different basis:

$$D\eta = \frac{\kappa T}{6\pi v} \quad (14)$$

where r is the radius of the diffusing particle. With $r \sim 3 \times 10^{-8}$ cm. one has $D\eta = \kappa T$ (1.8×10^6).

SUMMARY

Some properties of flow of solutes in and through rubbers are outlined. These properties indicate that, due to fluctuations of thermal energy, activated zones exist in certain polymers, of which viscous flow and diffusion are a consequence. A simple statistics of activated zones has been given, and from it equations are obtained for ΣN, D, D_s, and η, denoting respectively the total number of activated zones in rubber, the diffusion constant of simple solutes in the polymer, the self-diffusion constant of rubber, and its viscosity.

Functional relations are predicted between log D_o, log η_o, or ΔS^* (the entropy of activation) and the Arrhenius energy of activation for diffusion or viscous flow. The available data clearly demonstrate this relationship. They also indicate no discontinuity between rubbers and liquids as diffusion media.

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[19] In the subsequent treatment of viscous flow and diffusion, the simplest assumption will be made that E does not vary with zone size and, therefore, that Equation (4) may be employed.
[20] Or at different temperatures, the relationship exists between log D_o or log η_o and $E/(RT)$.
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[22] Barrer, *Trans. Faraday Soc.* **37**, 190 (1941); Barrer, "Diffusion in and through solids", Cambridge Univ. Press, **1941**, Chapters IX and X.
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THE INTERACTION BETWEEN RUBBER AND LIQUIDS

II. THE THERMODYNAMICAL BASIS OF THE SWELLING AND SOLUTION OF RUBBER *

G. GEE

48 TEWIN ROAD, WELWYN GARDEN CITY, HERTS., ENGLAND

The previous paper of this series[1] described an experimental study of the vapor pressures of benzene-rubber mixtures over the widest possible range of temperature and composition. The results were used to calculate Gibbs' free energies, heats and entropies of dilution Δg_o, Δh_o and Δs_o, where these quantities are defined as the net increase in Gibbs' free energy, heat content, and entropy consequent on mixing 1 gram of benzene with an infinite amount of rubber-benzene mixture. In the process of mixing 1 gram of rubber with an infinite amount of rubber-benzene mixture, the corresponding functions are the Gibbs' free energy, heat, and entropy of solution Δg_r, Δh_r, and Δs_r; these also were evaluated. It was shown that, except in dilute solution, all these functions were independent of the molecular weight of the rubber (over the range 40,000 to 280,000), and that the ratios $\Delta h_o/T\Delta s_o$ and $\Delta h_r/T\Delta s_r$ were of the order 0.4, 0.2, respectively, over most of the concentration range. The molecular heat of solution of normal raw rubber in benzene was found to be of the order of 5×10^5 cal., from which is was concluded that rubber dissolves in benzene only because of the very large entropy of solution. Some of these results throw doubt on the fundamental basis of the theories of solubility developed by Brønsted[2] and Schulz[3], and applied by them with considerable apparent success. It is the purpose of this paper to discuss the problem of solubility and swelling of rubber in a rather qualitative way, and to show that the behavior of rubber in critical mixtures of solvent and nonsolvent can be interpreted on the basis of the equations employed to describe the experimental data for rubber and benzene.

SWELLING AND SOLUTION

The work on benzene shows that the ready absorption of most organic liquids by rubber is not to be taken as evidence of any mutual affinity, but is due essentially to the large increase of entropy which results from mixing. Unless this large entropy increase is offset by a considerable absorption of heat, it must lead ultimately to complete solution of the rubber. The phenomenon of swelling which is so characteristic of rubber and other high-molecular substances affords a visual indication of the self-adhesion of the rubber chains. The condition for swelling to be observed is that the rate of absorption of liquid by rubber shall

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exceed the rate of dissolution of rubber in the liquid. In the case of a liquid in which rubber is soluble, this condition is fulfilled only when the molecular weight of the rubber is high; degraded rubbers disperse without preliminary swelling. Attention may be called to the general parallelism between the elastic and swelling properties of rubber fractions. It has been pointed out[4] that rubberlike elasticity can be observed only when the molecular chains adhere sufficiently strongly at certain points to prevent plastic flow. These adhesions or "entanglements" will evidently also resist dispersion in solvents, so that swelling, like high elasticity, is observed only when the molecular chains are long.

The vapor pressure data of Lens[5] and the swelling pressures measured by Posnjak[6] show that the free energies of dilution of rubber by various solvents differ by large factors. This is brought out by the different "apparent molecular weights" found by the application of osmotic methods in concentrated solutions[7]. The interpretation of these differences in terms of heats and entropies of mixing requires reliable vapor pressures over a temperature range, which are available only for rubber in benzene[1], toluene[8], and benzene+15% methanol[9]. These three solvents show large differences in heats of dilution, which may be illustrated by the values of the constant k in the expression: $\Delta h_o = k v_r^2$, which is found to fit the data for dilute solutions (v_r=volume fraction of rubber). The constants are: benzene 0.7, toluene 0.2, benzene+15% methanol 2.1. The entropies differ much less markedly, but the entropy of dilution of a rubber fraction of molecular weight 150,000 is approximately 50 per cent larger in benzene +15% methanol than in benzene. It should be noted that here and throughout this paper mixed solvents are treated as if they were pure liquids; it will be shown in a future communication that this is a valid approximation for dilute solutions. These results afford some support for the view, on which the following discussion is based, that differences in the entropies of mixing of rubber with various liquids may be neglected to a first approximation.

FORMULATION OF SOLUBILITY CONDITIONS

The problem of the solubility of rubber is essentially that of the miscibility of two liquids, and is capable of mathematical treatment if we can find an analytical expression for the Gibbs' free energy of dilution, Δg_o, as a function of T and v_r, the volume fraction of rubber in the mixture of rubber+liquid. At a sufficiently high temperature, $\left(\frac{\partial \Delta g_o}{\partial v_r}\right)_T$ is negative for all values of v_r, and the liquid and rubber will then be miscible in all proportions. At lower temperatures, two phases ^{c} and ^{d} will coexist in equilibrium if[10]:

$$\left.\begin{aligned} \Delta g_o^c &= \Delta g_o^d \\ \Delta g_r^c &= \Delta g_r^d \end{aligned}\right\} \qquad (1)$$

The critical solubility temperature T_c, above which only one phase can exist, is determined by the conditions[11]:

$$\left(\frac{\partial \Delta g_o}{\partial v_r}\right)_T = \left(\frac{\partial^2 \Delta g_o}{\partial v_r^2}\right)_T = 0 \qquad (2)$$

No precise analytical expression for Δg_o is at present available, but an approximate treatment will be given by making use of the results found for the

rubber+benzene system[1], which can be represented approximately by the following expressions for the heats and entropies of dilution and solution:

$$\left.\begin{aligned}\Delta h_o &= \alpha(1+\beta)\left(\frac{v_r}{1+\beta v_o}\right)\\ \Delta h_r &= \alpha(1+\beta)^2\left(\frac{v_o}{1+\beta v_o}\right)^2\end{aligned}\right\} \tag{3}$$

$$\left.\begin{aligned}\Delta s_r &= \frac{R}{M_e}\, v_o - \frac{R}{M_r}(\ln v_r + v_o)\\ \Delta s_o &= -\frac{R}{M_e}\left\{\ln v_o + v_r\left(1-\frac{M_e}{M_r}\right)\right\}\end{aligned}\right\} \tag{4}$$

where α, β are constants

M_r is the molecular weight of the rubber;
M_e is the molecular weight of an "element" of the rubber molecule.

Equation (4) differs from Flory's entropy equation[12] only by omission of the terms representing the disordering of the rubber structure. It must be emphasized that Flory's equation holds only approximately in the case of benzene, and values of Δs_o calculated from (4) may be in error by a factor of 3 or 4. The arithmetical results of the following analysis can, therefore, have only qualitative significance, and are given for illustrative purposes.

Combination of (2), (3) and (4) gives for the temperature T_c and volume fraction of the solvent v_{oc} at the critical solubility point[13], when $M_r \to \infty$

$$\left.\begin{aligned}T_c &= \frac{8}{27}\,\frac{\alpha}{\beta}\,(1+\beta)^2\,\frac{M_e}{R}\\ v_{oc} &= \frac{1}{2\beta}\end{aligned}\right\} \tag{5}$$

If two phases coexist, their compositions are to be found by combining Equations (1), (3) and (4). This leads to expressions which are too complicated for analytical solution, but which can be readily solved for particular values of the constants. The values actually employed were $\frac{M_e}{R}=50$, $\alpha=5$ cal. per g., $\beta=1$, and are believed to be of the right order of magnitude for mixtures of benzene and methanol, which show critical solubility behavior in the region of room temperature. For such solvents, preliminary osmotic data for dilute solutions ($v_o \simeq 1$) give $\frac{\Delta h_o}{v_r^2} \simeq 2.5$. This may be equated, by (3), to $\frac{\alpha}{1+\beta}$, while Equation (5) gives another relationship between α and β. With $\alpha=5$, $\beta=1$, we find $T_c=296$, $v_{oc}=0.50$; the latter is certainly too low, since the concentrated phase may frequently contain less than 50 per cent rubber[3]. Since different liquids are assumed to show the same entropy of mixing, the value of $\frac{M_e}{R}$ is taken from the data for benzene.

These constants have been inserted in Equations (3) and (4), and are used to calculate Δg_0 and Δg_r as functions of T and M_r. A typical family of curves is given in Figure 1, for $T=263$. Equation (1) can then be solved by reading from the curves the pair of values of v_r which give two equal values both of Δg_0 and Δg_r. The figures thus obtained from Figure 1 are summarized in Table I, together with values of the critical temperatures for rubbers of different molecular weights, obtained from Equation (2).

TABLE I

CRITICAL TEMPERATURES AND COMPOSITIONS OF PHASES AT $T = 263$

M_r	T_c	v_r^d at $T = 263°$	v_r^c at $T = 263°$
10^5	296	10^{-17}	0.84
2×10^4	293	2×10^{-4}	0.84
10^4	291	.007	0.84
5×10^3	290	.045	0.83_7
2×10^3	283	$.17_6$	0.81
10^3	273	$.33_5$	0.76_5

The results at other temperatures are summarized in Figure 2, in which log v_r^d

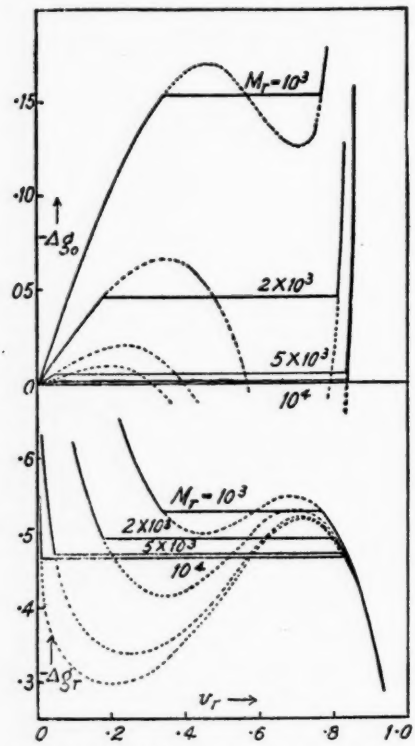

FIG. 1.—Calculation of solubility at $T = 263°$.

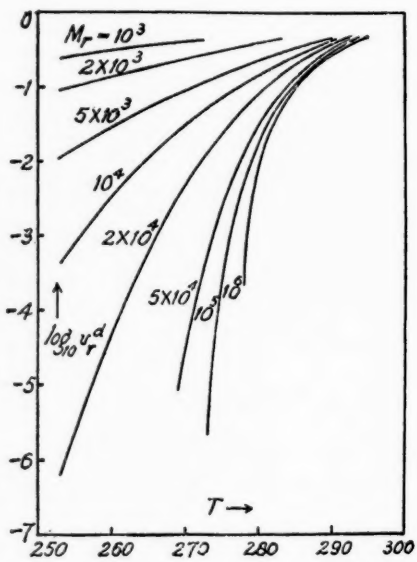

FIG. 2.—Effect of temperature on solubility.

is plotted against T, for a series of molecular weights. The principal conclusions from this analysis may be summarized as follows.

(1) For any liquid there is a critical temperature above which it is miscible in all proportions with rubber; this temperature is nearly independent of M_r unless M_r becomes small.

(2) The composition of the concentrated phase depends only slightly on M_r.

(3) The solubility—measured by v_r^d—depends greatly on the temperature, the coefficient rising somewhat with M_r. It is because of this fact that a liquid chosen at random normally appears to be either a nonsolvent or completely miscible with rubber, the temperature range in which the solubility is limited and measurable being confined to a few degrees.

There are few published data for rubber by which these conclusions may be tested, but they are in general agreement with the results of Brønsted and Volquartz[14], and Schulz[3] on polystyrene. The first part of (1) is not usually verifiable, since the critical solubility temperature for most pure liquids lies outside the range in which solubility measurements are feasible. This difficulty may be overcome by the use of mixtures of solvent and nonsolvent. By varying the proportions, the critical solution temperatures may be brought into a convenient range. In this case, however, a difficulty of interpretation arises from the fact that the solvent composition in the two phases will not, in general, be the same. Where the two liquids differ considerably (*e.g.*, a hydrocarbon and an alcohol), the distribution may be very unequal[14], and the approximation of treating the rubber-liquid system as binary is of questionable validity, but it must be made, pending completion of an extensive study of the system rubber—benzene—methanol now in progress. With this reservation, some preliminary data for the solubility of rubber in mixtures of benzene+methanol are given below, and will be seen to conform in a general way to the requirements of the theory.

SOLUBILITY OF RUBBER IN MIXTURES OF BENZENE AND METHANOL

Benzene+30% methanol was added from a burette to solutions of rubber in benzene+15% methanol until a turbidity was obtained which persisted on shaking. Benzene was then added until the turbidity disappeared. The compositions of the solution at these two points were calculated, and their mean taken as the true equilibrium value. The amount of hysteresis found in this way was small, *e.g.*, a 1 per cent solution of sol rubber at 52.5° C was precipitated by 20.8 per cent methanol and redissolved by 20.6 per cent methanol. The critical solubility temperatures for a number of rubbers in benzene+20% methanol were found by interpolating data obtained in this manner. The results are summarized in Table II. Except in the case of sol rubber, the temperature coefficient

TABLE II

CRITICAL SOLUBILITY TEMPERATURES IN BENZENE + 20% METHANOL

Substance	$10^{-3} M_r$	θ_1 (° C) 1% rubber	$\theta_{0.1}$ (° C) 0.1% rubber	$\theta_1 - \theta_{0.1}$ Obs.	$\theta_1 - \theta_{0.1}$ Fig. 2
Sol rubber	350	48	39.5	8.5	2
55/45 fraction	180	40	35	5	2
Degraded rubber 1.....	85	37.5	31.5	6	2.5
Degraded rubber 2 † ...	—	19.5	?	?	—
	15	26.5 *	9.5 *	17 *	6.5

* 21% methanol. † No. 2 was a fractionated product.

is seen to fall with decreasing molecular weight in approximately the way expected from the theory. The anomalous result for sol rubber probably arises from its lack of homogeneity, a similar phenomenon being shown by the data for benzene+ethanol given by Midgley, Henne and Renoll[15]. The small difference between the experimental and theoretical absolute values of $(\theta_1-\theta_{0.1})$ may also be due in part to this cause, but is actually no greater than might be expected from the approximations made in the theoretical analysis.

The effect of the composition of the (benzene+methanol) mixture is similar to that reported for polystyrene[3]. Thus the percentage of methanol is a linear function (a) of log v_r^d at constant T and M_r and (b) of $1/M_r$ at constant T and v_r^d. The interpretation of these results depends on the variation of the constants α, β with the solvent, and lies outside the scope of this paper. A linear variation of α with solvent composition (which is equivalent to Schulz' assumption) would be sufficient to account for the general result.

FRACTIONATION OF RUBBER

Rubber has been separated into a series of fractions by three types of method: (1) diffusion into a single solvent[16]; (2) dissolution in mixtures of solvent and nonsolvent containing progressively more solvent[17], and (3) fractional precipitation from solution by addition of a nonsolvent, or by cooling[15]. We are not concerned here with the first method, which makes use of the greater speed of solution of small molecules, to which reference has already been made. Whether such a method can ever be quantitative is open to question. Both the other methods depend on the establishment of an equilibrium in which the concentrated phase tends to contain the higher-molecular components.

In extending our analysis to the case of mixed rubbers, a new problem arises which does not seem to have been previously discussed. The formulation of the entropy of mixing of a liquid and two rubbers of different molecular weight requires us to find an expression for the entropy of mixing of the two rubbers. In so doing, Flory's expression for the entropy of mixing of long and short molecules[12] has been extended in the simplest possible way to a mixture of two rubbers of molecular weights M_{r^1} and M_{r^2} with a liquid. His equation differs from that for the "ideal" entropy of mixing in that volume fractions replace mole fractions. Assuming this relationship to be general, the net increase of entropy $\Delta s_{r^1}{}^{r\rightarrow m}$ when 1 gram of rubber of molecular weight M_{r^1} is transferred from a mixture ^{r} of the two rubbers, in which its volume fraction is $v_{r^1}{}^r$, to a large bulk of a ternary mixture ^{m} in which it is $v_{r^1}{}^m$, is found to be:

$$\Delta s_{r^1}{}^{r\rightarrow m}=\frac{R}{M_e}\,v_0{}^m+\frac{R}{M_{r^1}}\left(\ln\frac{v_{r^1}{}^r}{v_{r^1}{}^m}+v_{r^1}{}^m-v_{r^1}{}^r\right)+\frac{R}{M_{r^2}}\left(v_{r^2}{}^m-v_{r^2}{}^r\right) \qquad (6)$$

The entropy of dilution is:

$$\Delta s_0=\frac{R}{M_e}\left(\ln\frac{1}{v_0{}^m}+v_0{}^m-1\right)+R\left(\frac{v_{r^1}{}^m}{M_{r^1}}+\frac{v_{r^2}{}^m}{M_{r^2}}\right) \qquad (7)$$

The complete solution of Equations (1), (3), (6) and (7) would be somewhat laborious, but some interesting features are readily deduced. Since the heat of solution is independent of the molecular weight, it is easily shown that if two ternary phases ^{c} and ^{d} are in equilibrium with respect to the two rubbers, the

difference between the entropies of solution of the two rubbers must be the same for each phase. Applying this condition to Equation (6) leads to the result:

$$\frac{v_{r^2}^c}{v_{r^2}^d} = \left(\frac{v_{r^1}^c}{v_{r^1}^d}\right) M_{r^2}/M_{r^1} \tag{8}$$

Since $v_{r^1}^c + v_{r^2}^c = 1 - v_o^c$, which we have shown to be nearly independent of M_r, Equation (8) enables us to calculate the composition of the concentrated phase in equilibrium with a given solution. Some typical results are given in Table III, for 2 values of v_o^c.

TABLE III

DISTRIBUTION OF TWO RUBBERS BETWEEN TWO PHASES

$v_{r^1}^d + v_{r^2}^d$	$v_{r^2}^d/v_{r^1}^d$	M_{r^2}/M_{r^1}	$v_{r^2}^c/v_{r^1}^c$ ($v_o^c = 0.2$)	$v_{r^2}^c/v_{r^1}^c$ ($v_o^c = 0.8$)
0.004	1	2	19.5	9.5
0.02	1	2	8.5	4.0
0.10	1	2	3.5	1.56
0.006	0.2	2	5.1	2.4
0.02	1	10	51	13.9

Table III leads to two general results of practical interest in the fractionation of rubber:

(1) The efficiency of separation should be greatly improved by the use of dilute solutions.

(2) No single-stage fractionation, whether by dissolution or precipitation, can give anything approaching complete separation of rubber, whose molecular weight differs by a factor of less than two.

Both these conclusions are borne out by our general experience, but no data are at present available for a quantitative test of Equation (8).

The application of these results to rubber containing a continuous distribution of molecular weights presents the difficulty of deciding what band width is to define an "individual" species. The above equation for the entropy of mixing assumes the rubbers to behave as separate liquids: the extent to which this holds will determine both the validity of the present treatment and the degree of separation attainable by repeated fractionations.

CONCLUSIONS

It has been the purpose of this paper to show that the general phenomena of solubility and swelling of rubber could be understood on the basis of the detailed results found experimentally for the rubber-benzene system. Using no arbitrary constants which cannot be related to experiment, temperature coefficients of solubility of the right order of magnitude are calculated. It is clear that the qualitative agreement of this treatment with the meagre experimental data at present available must not be taken as evidence of the accuracy in detail of the equations employed for the heat and entropy of solution.

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THE INFLUENCE OF CHEMICAL STRUCTURE ON THE IMBIBITION OF LIQUIDS BY RUBBER. I*

G. S. WHITBY, A. B. A. EVANS and D. S. PASTERNACK

DEPARTMENT OF CHEMISTRY, MCGILL UNIVERSITY, MONTREAL, CANADA

Studies of the swelling of rubber which had been carried out up to 1924 were reviewed by one of the authors in an earlier publication[1]. A review of subsequent studies is to be found in a paper by Scott[2], who himself has contributed some data on the subject. These prior studies were not, however, concerned primarily to secure systematic information on the influence of the chemical structure of liquids on their imbibition by rubber, and they involved only a relatively small number of liquids, except for the study by Lee[3], in which the behavior of raw rubber in sixty-nine liquids was observed only qualitatively. Further, a good many of the earlier observers used material of unknown history and composition, such as "black rubber tubing", and often assuming the swelling to reach a maximum in twenty-four hours.

In the present study the course of the swelling of rubber, both raw and vulcanized, has been followed, quantitatively, at intervals over long periods, and a very large number of liquids have been examined. The present installment deals largely with classes of liquids (acids, alcohols, aldehydes, ketones, etc.) containing the more highly polar groups. A collection of hydrocarbons is, however, included, because hydrocarbons are in general good swelling agents, and data on them will serve for comparison with that on other classes of compounds.

Data are given in the table. They may be left largely to speak for themselves. Only some of the broad generalizations which they indicate, and some of the more interesting salient features which they present, will be specified.

1. There is, speaking very broadly, a parallelism between the degree of swelling of raw and of vulcanized rubber in any liquid. Imbibition by vulcanized rubber is usually considerably less than by raw rubber, although there are a few exceptions. For the quantitative comparison of various liquids the data on vulcanized rubber are generally more valuable than those on raw rubber because, in good swelling agents, raw rubber gradually disperses and, accordingly, the maximum imbibition value and true course of the swelling curve may be masked by some of the rubber passing into solution. In the case of liquids of low swelling power, it may be best to use for comparison the data on raw rubber.

2. In no case does the imbibition come to a sharp maximum within the period of observation. Whereas in some cases the increase is relatively slight after twenty-four hours, in others it is quite large. The rate of imbibition does not seem to bear any clear relation to the viscosity of the liquids (even of the same chemical class) involved.

3. The steadily progressive nature of the swelling process is indicated by the

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fact that in not a few cases it was observed that even vulcanized rubber had undergone dispersion after three and one-half years, during which time the samples had been kept immersed, in the dark in corked test-tubes. Only a limited number of the samples were kept for this long period and then examined, and it may be assumed that more samples than the number actually noted would have become dispersed over such a period. The solutions of vulcanized rubber did not differ much in viscosity from the viscosity of the liquids concerned. It may be, of course, that the small amount of oxygen in the tubes was a factor in producing dispersion.

4. The most interesting feature of the results is perhaps the fact that, in a homologous series of compounds containing a polar group, it is not usually necessary to proceed far along in the series before encountering substances which are solvents for raw, and good swelling agents for vulcanized, rubber, even though the lowest members of the series may be precipitants for rubber. Thus, for example, whereas acetone precipitates raw rubber from its solutions, diethylketone is a solvent for it; whereas acetic acid and acetaldehyde are imbibed only very slightly, butyric acid and butyraldehyde will dissolve raw rubber; whereas acetophenone does not produce sufficient swelling to dissolve raw rubber, butyrophenone does.

In the series of the most highly polar compounds, however, such alcohols and nitriles, the change from precipitants in the lowest members to good swelling agents in the higher members is slower, and in no member of the aliphatic series was swelling high enough to lead to dispersion: even octyl alcohol failed to dissolve raw rubber.

In general, however, except in the case of classes of compounds containing the most highly polar groups, such as OH or CN, a very moderate increase in the length of the attached carbon chains is sufficient to reduce the polarity to a degree at which there is high imbibition by rubber hydrocarbon.

5. The highly unfavorable effect of the OH group on imbibition may be seen strikingly by comparing lactic acid with propionic acid; ricinoleic acid with oleic acid; dichlorhydrin with trichlorohydrin; mesityl oxide with methylisobutylketone, and so on. Or, again, in the high swelling power of the acid chlorides (RCOCl) compared with the acids (RCOOH). When two acid chloride groups are present, as in oxalyl chloride, swelling is still further enhanced compared with that in the acid chlorides of monocarboxylic acids.

The replacement of the carboxylic hydroxyl by the sulfhydryl group (as in thioacetic acid) has an even more marked effect in raising imbibition than its replacement by chlorine (as in acetyl chloride). On the other hand, the sulfhydryl group, like the hydroxyl group, in the alkyl chain reduces imbibition (*cf.* thioglycollic acid and acetic acid). When attached to the benzene nucleus, however, SH greatly enhances swelling, thiophenol being a much more powerful swelling agent than phenol and indeed more powerful than benzene. This is significant in connection with the present practice of using aromatic mercaptans as softening agents in rubber stocks.

6. The introduction of chlorine into the molecule usually leads to markedly increased swelling power, as may be seen by a comparison of dichloroacetic acid with acetic acid; chloral with acetaldehyde; chlorophenols with phenol, and so on.

7. Polar groups seem often to have a much less unfavorable effect on the degree of swelling when they are attached directly to aromatic nuclei than when they occur in aliphatic chains. This is seen perhaps in the aldehydes, the nitro compounds and certainly the nitriles. The aromatic nitriles, although

having high dielectric constants, are good swelling agents for vulcanized rubber and dissolve raw rubber. Phenylacetonitrile, on the other hand, swells rubber hardly at all.

8. Mustard oils, although possessed of relatively high dielectric constants, have high swelling power.

9. In the hydrocarbon collection the data show the aliphatic hydrocarbons to be in general less powerful swelling agents than the aromatic or hydroaromatic ones. This is in accord with general experience in the rubber industry. Unsaturation seems to increase swelling, as a comparison of 1-pentene with *n*-pentane, and of biallyl with *n*-hexane indicates.

10. The existence of solvents for raw rubber among inorganic compounds is interesting. Both silicon tetrachloride and tin tetrachloride swell and dissolve raw rubber, although, in that order, they are less powerful agents than carbon tetrachloride. Arsenic trichloride is a strong swelling agent for raw rubber, and produces a purple color, due to reaction with the sterols in rubber[4].

11. Wo. Ostwald[5], from a consideration of swelling data for a very limited number of liquids, suggested that the imbibition of liquids by rubber was related inversely to their dielectric constants in accord with the equation: $\sqrt[n]{QD}=k$, where Q is the maximum imbibition, D, the dielectric constant, and n a constant between 2 and 3. The present, more extensive data show that no such relationship can be substantiated. In a strictly homologous series of organic compounds imbibition is usually in the order of diminishing dielectric constant, but is not quantitatively related to the latter. But when compounds of different classes or even of the same class, but in different homologous series, are considered, the dielectric constant provides only the roughest guide to swelling power; it is no reliable guide, and there is no precise relationship.

12. Considered most broadly, the data create the impression that, just as the ability of liquids to dissolve crystalline substances implies that the solvent is not too remote in character from the solute, so the ability of liquids to swell rubber implies that such liquids are not too remote in type from rubber hydrocarbon. Accordingly, they create the impression that the swelling of an organic colloid, such as rubber, is basically a process analogous to the solution of a crystalline substance[6].

EXPERIMENTAL

The raw rubber samples were all taken from the same sheet of smoked sheet, of specific gravity 0.9146 at room temperature. Each sample consisted of a strip of approximately $1.5\times0.3\times0.2$ cm., weighing approximately 0.10 gram. The vulcanized rubber samples were taken from sheets prepared by curing a 90:10 rubber:sulfur stock in a mould at 148° C, for 75 minutes in an oil bath. Each sample consisted of a strip about $1.3\times0.5\times0.2$ cm., and weighed about 0.11 gram. The specific gravity at room temperature was 0.9820.

Weighed strips of dried rubber were placed in the various liquids in dried, corked test-tubes. After intervals, in the dark, of 1, 2, 3, 7, 31, 62 and in some cases 93 days, the strips were removed by a wire hook, and dropped into a weighed weighing bottle lined with filter paper. The stopper was at once inserted, the bottle was rolled round to remove liquid adhering to the rubber, the filter paper was quickly removed, the stopper inserted, and the weight noted. The swollen strip was then returned to the liquid. For purposes of comparison, the procedure is sufficiently accurate, as duplicate experiments showed that the

Swelling of Rubber in Various Liquids

Liquid	D.K.	cc. of liquid imbibed per cc. of rubber: Vulcanized (days) 1	2	3	7	31	62	Raw (days) 1	2	3	7	31	62
Hydrocarbons													
n-Pentane	1.83	1.16	1.12	1.04	1.10	—	—	6.67	7.95	8.63	9.72*	—	—
n-Hexane	1.87	1.18	1.18	—	1.15	—	—	—	15.78*	—	—	—	—
n-Octane	1.94	2.36	2.31	2.33	2.43	2.67	2.85	—	—	—	—	—	—
1-Pentene	2.07	2.14	2.23	2.30	2.33	—	—	†	—	—	—	—	—
1, 5-Hexadiene (biallyl)	—	2.19	2.24	2.16	2.29	2.44	—	14.58*	—	—	—	—	—
Benzene	2.28	4.02	4.06	4.21	4.50	5.00	‖	26.08*	—	—	—	—	—
Toluene	2.39	4.17	4.36	4.39	4.62	4.84	—	28.25*	—	—	—	—	—
m-Xylene	2.37	4.17	4.20	4.28	4.29	4.17	—	—	—	—	—	—	—
Mesitylene	2.35	3.30	3.41	3.49	3.67	4.11	—	20.47*	—	—	—	—	—
Methylcyclohexane	—	2.60	2.60	2.58	2.56	2.80	—	28.70*†	—	—	—	—	—
Tetrahydronaphthalene	—	4.87	5.21	5.50	6.31	—	—	16.65§	*	—	—	—	—
Limonene	2.36	4.18	4.40	4.58	5.00	6.94	—	‡	—	—	—	—	—
Phellandrene	—	3.28	4.24	5.80	—	—	—	9.21§	*	—	—	—	—
d-Pinene	2.60	2.94	2.94	2.99	3.02	3.83	—	18.64	20.24*	—	—	—	—
Cedrene	—	2.73	3.11	3.32	3.42	3.83	—	5.27	7.90*	—	—	—	—
Acids													
Formic acid	4.7	0.12	0.14	0.15	0.21	0.31	—	0.33	0.42	0.47	0.62	0.80	—
Acetic acid	6.4	0.14	0.15	0.16	0.18	0.20	—	0.22	0.27	0.33	0.45	0.43	—
Propionic acid	3.19	—	—	—	—	—	—	—	—	0.62	0.69	—	—
n-Butyric acid	2.85	1.57	1.61	1.62	1.70	2.23	—	3.31	4.08	4.23	4.33	3.23*	—
n-Valeric acid	2.6	1.49	1.59	1.61	1.69	—	‖	4.40	5.67	5.96	3.88*	—	—
n-Caproic acid	3.2	1.65	1.76	1.77	1.94	3.63	—	4.32	6.37	7.07	6.75*	—	—
n-Heptoic acid	—	1.97	1.99	2.06	2.20	5.06	‖	5.19	7.00	7.20	5.82*	1.32*	—
Caprylic acid	3.2	1.94	1.97	2.03	2.23	4.46	—	4.72	6.43	7.63	6.68*	*	—
Pelargonic acid	—	1.62	1.76	1.91	2.04	3.29	—	3.41	5.06	6.57	6.99	1.60*	—
Undecylenic acid	—	—	1.38	1.73	2.67	—	—	1.90	3.25	4.08	3.44*	—	—
Oleic acid	2.45	0.46	0.70	0.88	1.39	2.33	—	1.48	2.35	2.87	4.55	5.08*	—
Linoleic acid	—	0.58	0.80	0.95	1.30	2.25	—	1.47	2.04	2.45	3.54	4.60*	—
Linolenic acid (under CO_2)	—	0.82	1.29	1.47	1.94	2.11	—	2.17	3.50	4.47	6.61	5.54*	—
Ricinoleic acid	—	0.23	0.23	0.24	0.26	0.39	—	0.13	0.17	0.10	0.11	0.19	—
Lactic acid	23	—	0.02	0.03	0.02	—	—	—	—	0.04	0.04	—	—
Levulinic acid	—	0.06	0.06	0.07	0.07	0.11	—	0.09	0.06	0.07	0.09	0.15	—
Dichloroacetic acid	8.2	4.91	8.88	11.17	12.17	†	—	4.60*	8.22	9.86	—	—	—
Thioacetic acid	13.0	3.97	4.69	5.09	6.28	7.50	—	3.78	3.59	3.42	3.23*	—	—
Thioglycollic acid	—	0.09	0.10	—	0.20	—	—	0.16	0.17	0.18	0.19	0.11	—
Naphthenic acids	—	—	—	—	—	—	—	1.74	—	3.09	4.50§	—	—
n-Butyric acid	—	1.43	1.71	2.09	3.22	—	—	†	—	—	—	—	—
Capric acid	—	1.54	1.75	2.02	2.13	—	—	3.92*	—	—	—	—	—
Undecylic acid	—	1.50	1.73	1.97	2.70	—	—	3.85*	—	—	—	—	—
Lauric acid	—	1.21	1.55	1.84	2.77	—	—	4.05*	—	—	—	—	—
Acid Anhydrides													
Acetic anhydride	20.5	—	0.05	—	0.07	—	—	0.03	—	—	0.12	—	—
Propionic anhydride	18	0.55	0.58	0.58	0.61	0.81	—	0.50	0.57	0.61	0.62	—	—
n-Valeric anhydride	—	1.14	1.26	1.31	1.85	—	‖	1.95	2.58	3.11	3.58	—	—

All determinations at room temperature (approximately 20° C), except those with liquids printed in italics which were at 58° C.

† Disintegrating.

‡ In solution, or nearly so.

§ Beginning to disperse, as shown by the fact that the liquid gives a turbidity when treated with alcohol.

* Considerable rubber has dispersed, as shown by the fact that the liquid gives a heavy precipitate when treated with alcohol.

‖ In solution after 3.5 years.

D.K. Dielectric constant.

SWELLING OF RUBBER IN VARIOUS LIQUIDS—*Continued*

Liquid	D.K.	cc. of liquid imbibed per cc. of rubber: Vulcanized (days) 1	2	3	7	31	62	Raw (days) 1	2	3	7	31	62
ACID CHLORIDES													
Acetyl chloride	15.9	4.67	5.30	5.48	4.98	—	—	2.60*	—	—	—	—	—
Propionyl chloride	—	2.90	3.58	3.98	4.29	—	—	5.85	3.61*	‡	—	—	—
Butyryl chloride	—	2.58	2.93	3.08	3.77	5.16	—	‡	—	—	—	—	—
Capronyl chloride	—	3.22	3.44	3.51	3.60	2.42	—	9.73*	—	—	—	—	—
Oxalyl chloride	—	4.24	4.70	5.20	6.91	8.30	8.57	9.38*	6.40	5.19	—	—	—
Benzoyl chloride	19	3.07	3.39	3.58	4.16	6.21	—	7.14*	‡	—	—	—	—
o-Chlorobenzoyl chloride	—	3.07	3.35	3.52	3.82	4.69	5.25	7.21	8.33*	7.31	3.90	—	—
p-Chlorobenzoyl chloride	—	3.22	3.44	3.56	3.94	4.82	5.55	8.37*	—	—	—	—	—
Benzenesulfonyl chloride	—	—	—	1.54	1.66	—	—	—	—	—	—	—	—
ALDEHYDES													
Acetaldehyde	21.6	—	0.19	—	0.21	—	—	0.23	—	—	0.49	—	—
Propionaldehyde	18	0.64	0.67	0.66	0.74	—	—	—	—	—	—	—	—
n-Butyraldehyde	13.5	1.44	1.55	—	1.83	—	—	8.22	8.70*	—	2.58	—	—
n-Valeraldehyde	10	1.24	1.32	1.40	1.59	1.89	—	4.61	5.05	4.91	4.43*	1.07	—
n-Heptaldehyde	—	1.65	1.78	—	2.22	—	—	—	6.32	3.94*	—	—	—
Benzaldehyde	18.0	1.48	1.57	1.68	1.73	3.25	—	1.23	1.29	1.26	1.27	1.06§	—
o-Tolualdehyde	—	1.84	1.86	1.98	2.40	4.5	5.38‖	3.30	4.18	4.39	3.59*	1.48	—
p-Tolualdehyde	—	1.60	1.67	1.70	1.81	2.17	2.48	2.54	3.22	3.72	3.80	2.16*	—
Phenylacetaldehyde	4.87	0.33	0.42	0.48	0.60	1.36	—	—	—	—	—	—	—
o-Chlorobenzaldehyde	—	2.17	2.26	2.30	2.34	2.60	2.82‖	5.36	6.55	6.60	4.41*	2.12	—
Anisaldehyde	16	0.17	0.19	0.22	0.26	0.27	—	—	—	—	—	—	—
o-Methoxybenzaldehyde	—	0.46	0.54	0.56	0.60	—	—	—	—	—	—	—	—
Salicylaldehyde	13.9	0.86	0.91	0.92	0.92	1.02	—	0.46	0.50	0.50	0.50	0.50	—
Cinnamic aldehyde	—	—	—	—	—	—	—	0.12	0.13	0.12	0.14	0.15	—
Chloral	6.67	3.72	3.80	3.83	3.96	—	—	—	—	—	—	—	—
Paraldehyde	14.5	0.88	0.95	0.96	1.01	1.15	—	0.93	0.98	0.98	1.01	1.16	—
Crotonaldehyde	—	0.75	0.85	—	0.97	—	—	0.47	0.56	—	1.08	—	—
Citral	—	0.20	0.28	0.28	0.34	0.58	—	0.26	0.28	0.28	0.31	0.43	—
o-Chlorobenzaldehyde	—	3.78	4.88	—	—	—	—	—	—	—	—	—	—
p-Chlorobenzaldehyde	—	5.82	8.02	—	—	—	—	—	—	—	—	—	—
KETONES													
Acetone	21.4	—	—	0.03	0.03	—	—	—	—	—	0.05	—	—
Methylethylketone	17.8	0.72	0.73	0.77	0.87	1.01	—	0.70	0.66	0.68	0.67	0.67	—
Diethylketone	17.0	1.52	1.58	1.63	1.83	—	—	7.35	6.77	—	0.96*	—	—
Ethylpropylketone	—	2.10	2.15	2.22	2.45	4.97	8.02‖	8.10	7.05	5.75*	3.13	—	—
Diisopropylketone	12	1.85	2.03	2.17	2.67	4.06	—	5.61§	1.85*	1.12	—	—	—
Methylisobutylketone	12.2	0.89	0.93	—	1.02	—	—	—	2.36	2.52	2.23*	—	—
Acetophenone	18.3	1.21	1.28	1.29	1.40	3.90	5.10	0.63	—	0.66	0.69	0.70	—
Propiophenone	15.5	1.54	1.61	1.67	1.90	3.11	4.42‖	1.86	2.37	2.50	2.52	2.53	—
Butyrophenone	—	1.99	2.14	2.22	2.28	2.51	2.67	4.80	5.91	6.15	4.27*	—	1.58
Methyl-*p*-tolylketone	—	1.33	1.34	1.39	1.47	2.03	‖	0.91	1.11	1.12	—	—	—
Mesityl oxide	15.4	0.22	0.25	0.26	0.30	0.36	—	0.22	0.23	0.25	0.32	0.58	—
Methylheptenone	—	0.29	0.34	0.38	0.43	0.85	—	—	—	—	—	—	—
Cyclohexanone	—	2.67	3.01	3.26	4.80	8.70	12.61‖	6.55	5.16*	3.02	1.49	—	—
ALCOHOLS, ETC.													
n-Propyl alcohol	21.8	0.02	0.02	0.02	0.02	—	—	0.01	0.01	0.03	0.05	—	—
tert.-Butyl alcohol	11.4	0.12	0.12	0.14	0.19	0.21	0.21	0.13	0.14	0.17	0.16	0.19	0.17
Amyl alcohol	15	0.06	0.07	0.08	0.09	—	—	0.11	0.11	0.11	0.12	—	—
n-Hexyl alcohol	—	0.14	0.17	0.19	0.21	0.37	0.54‖	0.22	0.25	0.28	0.25	0.26	0.26
n-Heptyl alcohol	6.7	0.60	0.66	0.72	0.76	1.14	1.46	0.94	1.14	1.22	1.20	—	1.26
prim.-*n*-Octyl alcohol	3.4	0.75	0.86	0.91	0.98	1.97	—	0.72	0.98	1.07	1.22	1.08	—

SWELLING OF RUBBER IN VARIOUS LIQUIDS—*Continued*

Liquid	D.K.	cc. of liquid imbibed per cc. of rubber: Vulcanized (days) 1	2	3	7	31	62	Raw (days) 1	2	3	7	31	62
ALCOHOLS, ETC.—*Cont.*													
sec.-*n*-Octyl alcohol	—	0.58	0.64	0.68	0.69	0.94	1.24	0.95	1.20	1.30	1.36	1.41	—
Allyl alcohol	20.6	—	—	—	—	—	—	0.04	0.04	0.04	0.05	—	—
Benzyl alcohol	13.0	0.29	0.32	0.35	0.37	0.66	—	0.09	0.08	0.09	0.12	0.16	—
m-Cresol	10.3	0.87	1.12	1.28	1.44	1.64	—	0.16	0.22	0.25	0.35	0.48	—
m-Chloro-*p*-cresol	—	1.35	1.75	1.88	1.96	2.08	2.14	1.31	1.61	1.72	1.80	—	2.67
Cyclohexanol	15	0.41	0.59	0.76	1.27	1.59	—	0.60	0.86	1.07	1.58	2.29	—
3-Methylcyclohexanol	—	0.50	0.71	0.88	1.20	1.74	2.72‖	1.20	1.75	2.37	3.54	5.40§	5.31
Diacetone alcohol	—	0.56	0.57	0.58	0.70	0.80	—	—	—	1.15	1.17	—	—
Trimethyleneglycol	—	0.06	0.06	0.06	0.05	—	—	0.08	0.11	0.10	0.10	—	—
Geraniol	—	0.40	0.55	0.65	0.84	1.10	—	0.60	0.80	0.92	1.16	1.35	—
Citronellol	—	0.78	0.95	1.15	1.30	2.56	—	—	—	—	—	—	—
Thiophenol	—	4.35	4.79	5.20	6.34	12.60	—	—	—	—	—	—	—
Thio-α-naphthol	—	1.44	1.81	2.25	3.27	—	—	0.80	1.42	1.37	1.87	—	—
tert.-Butyl alcohol	11.4	0.29	0.36	0.35	—	—	—	—	—	—	—	—	—
Lauryl alcohol	—	0.92	1.20	1.31	—	—	—	—	—	—	—	—	—
Cetyl alcohol	—	1.18	1.95	2.32	—	—	—	—	—	—	—	—	—
Phenol	—	0.45	—	0.52	0.63	—	—	—	—	—	—	—	—
o-Chlorophenol	8	4.82	5.09	—	—	—	—	—	—	—	—	—	—
m-Chlorophenol	—	4.95	5.75	—	—	—	—	—	—	—	—	—	—
p-Chlorophenol	—	3.61	4.16	—	—	—	—	—	—	—	—	—	—
NITRILES													
Acetonitrile	38.8	0.04	0.04	0.04	0.04	0.04	—	0.02	0.02	0.02	0.02	0.02	—
Propionitrile	27.7	0.06	0.06	0.06	0.05	0.08	0.10	0.08	0.07	0.07	0.06	0.07	0.06
Capronitrile	15.5	0.68	0.71	0.72	0.80	—	—	—	—	—	0.75	—	—
Phenylacetonitrile	—	0.16	0.19	0.20	0.21	0.22	—	0.07	0.07	0.07	0.07	0.07	—
Benzonitrile	26.5	2.08	2.16	2.21	2.36	2.64	—	3.00	3.94	4.74	5.52	5.85*	—
o-Tolunitrile	18.6	2.12	2.14	2.18	2.22	2.28	2.46	5.21	6.41	7.03	6.62	4.34*	3.10
MUSTARD OILS, ETC.													
Ethyl mustard oil	19.7	2.35	2.39	2.48	2.71	4.07	—	10.00*	‡	—	—	—	—
Allyl mustard oil	17.3	2.24	2.46	2.68	2.97	3.42	—	6.73	8.68	8.64§	5.09*	2.54	—
Phenyl mustard oil	10.7	2.70	2.77	2.80	3.16	4.46	—	12.16*	—	—	—	—	—
o-Tolyl mustard oil	—	3.48	3.51	3.51	3.52	3.83	‖	14.02	18.62	20.22	15.30*	9.13	—
n-Butyl thiocyanate	—	1.85	1.87	1.90	1.92	3.86	‖	5.71	6.66	6.85	6.24*	4.15	3.22
Phenyl isocyanate	8.9	2.81	2.97	3.10	3.26	3.72	—	6.39*	—	—	—	—	—
NITRO COMPOUNDS													
Nitromethane	39.4	0.03	0.03	0.03	0.04	0.05	0.05	0.06	0.06	0.06	0.05	0.05	0.05
Tetranitromethane	2.13	0.05	—	—	—	—	—	—	—	—	—	—	—
Nitrobenzene	36.45	—	1.20	—	1.13	—	—	1.01	1.16	1.18	1.22	—	—
o-Nitrotoluene	27.7	—	1.78	—	1.94	—	—	1.06	1.36	—	1.78	—	—
CHLORHYDRINS													
Ethylene chlorhydrin	—	0.13	0.15	0.17	0.23	0.37	—	0.10	0.11	0.14	0.19	0.40	—
Epichlorhydrin	—	0.07	0.15	0.16	0.17	—	—	0.12	0.13	—	0.14	—	—
α,α′-Dichlorhydrin	—	0.06	—	0.08	—	—	—	0.08	0.09	—	0.13	—	—
Trichlorhydrin	—	2.91	3.20	3.32	3.62	—	—	5.82	*	—	—	—	—
β-Butyrodichlorhydrin	—	0.89	1.18	1.25	1.46	3.15	—	0.91	1.08	1.17	1.27	1.37§	—
INORGANIC HALIDES													
Silicon tetrachloride	2.40	0.08	0.59	2.20	1.88	2.05	—	13.64	11.50	12.07	2.79*	‡	—
Tin tetrachloride	3.2	0.47	0.53	0.59	0.66	0.69	0.70	2.29	2.16*	2.00	1.68	1.18	1.04
Arsenic trichloride	12.8	—	—	—	—	—	—	34.0*	—	—	—	—	—

first place of decimals is reliable, and that in some cases the second place could be reproduced almost exactly.

In the case of liquids liable to decomposition by atmospheric moisture (acid and inorganic chlorides), it was necessary to deviate from the procedure by using a separate strip of rubber for each period. In these cases the purified liquid was distilled into the tubes, which were then sealed. In the case of experiments at elevated temperature, the filter paper and the weighing bottle were warmed before the swollen strip was introduced.

The authors thank F. McI. Smith for assistance in the earlier stages of these studies.

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[4] Whitby, *Biochem. J.* **17**, 8 (1923).
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CHEMICAL REACTIONS DURING VULCANIZATION. III *

E. A. HAUSER and M. C. SZE

DEPARTMENT OF CHEMICAL ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS

The chemical reactions which take place in the vulcanization of soft rubber at elevated temperatures, with both accelerated and nonaccelerated simple rubber-sulfur compounds, have been discussed recently by Hauser and Brown.[1] A broadening of their scope to include vulcanization to the hard or ebonite stage and a study of the chemical reactions in the formation of factice from unsaturated vegetable oils at elevated temperatures was considered necessary to the development of a theory of sulfur vulcanization at elevated temperatures which would embrace all known facts.

Vulcanization of rubber to the ebonite stage was carried out with two compounds, one containing rubber, sulfur and zinc oxide, the other containing rubber, sulfur, and the organic accelerator diphenylguanidine.

Tung oil and linseed oil were used as typical unsaturated vegetable oils in the production of factice.

EXPERIMENTAL PROCEDURE

Vulcanization of tung and linseed oils was carried out at a constant temperature of 150°C in an inert atmosphere of carbon dioxide to prevent any side oxidation reaction. Standard test-slabs were vulcanized to hard rubber in a platen press maintained at 150°C. Samples were heated for various periods of time, and were then analyzed.

Combined sulfur was determined as the difference between total and free sulfur. With samples containing zinc oxide, a correction was applied to account for the sulfur converted to zinc sulfide. Total sulfur was determined by the method of Water and Tuttle,[2] and free sulfur by the procedure suggested by Oldham, Baker and Craytor.[3] The proportion of sulfur present as metallic sulfide was estimated according to the method of Stevens.[4]

The amounts of hydrogen sulfide formed during the vulcanization of tung and linseed oils were estimated by the differences between the analytically determined total sulfurs and the quantities of sulfur added to the oil before vulcanization. The liberation of hydrogen sulfide was qualitatively confirmed by the blackening of wet lead-acetate paper in the effluent carbon dioxide gas which was used as the inert atmosphere during vulcanization.

The unsaturation of linseed oil was measured according to the usual Hanus procedure.[5] With hard rubber vulcanizates, unsaturation was measured by the iodine chloride absorption method of Kemp,[6] as modified by Blake and Bruce,[7] using *p*-dichlorobenzene as the solvent.

The measurement of the total unsaturation of tung oil is a problem which has hitherto not been completely solved. Conventional methods of oil analysis are

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known to measure only two of the three conjugated double bonds of the eleostearic acid in tung oil. However, in the present study of factice formation, it was essential to have a method by which all three conjugated double bonds of eleostearic acid could be measured. Holde, Blevberg, and Aziz [8] claim that, by the use of iodine bromide dissolved in sufficient excess and by a long enough time of contact, all three double bonds of eleostearic acid can be saturated. A series of preliminary experiments demonstrated that the effect of time became insignificant after 2 hours of reaction. However, the quantity of excess reagent used had a very pronounced effect, similar to what had been found with the standard Wijs procedure when applied to the same oil.[9] The experimental data showing the influence of excess reagent are presented in Figure 1. To use this new method for measurements of unsaturation, a definite set of conditions had to be established. The time of reaction was set at 2 hours, at a temperature of 25°C. To determine how much excess reagent should be used to obtain the correct unsaturation, the true total iodine number of the oil had to be known.

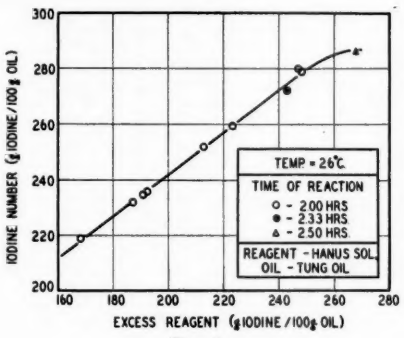


FIG. 1.

Therefore, an analysis of the oil was made to determine its content of eleostearic acid.[10]. From the Wijs iodine number and eleostearic acid content, the true unsaturation of the oil was calculated to be 234.4 grams of iodine per 100 grams of oil. From Figure 1 we find that the excess reagent should be 190 grams of iodine per 100 grams of oil, or an excess of approximately 80 per cent.[11]

It is believed that this new method [12] is more valuable than the standard Wijs procedure for oil analysis, as it gives the total rather than the partial unsaturation of tung oil.

Two additional measurements were made on tung oil vulcanizates, viz., specific gravity and diene number (a measure of the conjugated double bonds). The specific gravity was measured with a pycnometer. The maleic anhydride condensation method of Ellis and Jones [10] was used to determine the diene number, which was expressed in terms of iodine, with two atoms of iodine equivalent to two double bonds in conjugation.

THE FORMATION OF FACTICE

Data on the vulcanization of tung oil are presented in Figure 2. To facilitate their interpretation, the results are replotted *versus* combined sulfur in Figure 3. From Figure 3 it can be seen that, while combined sulfur increases and the iodine number decreases, the diene number, measured by condensation with

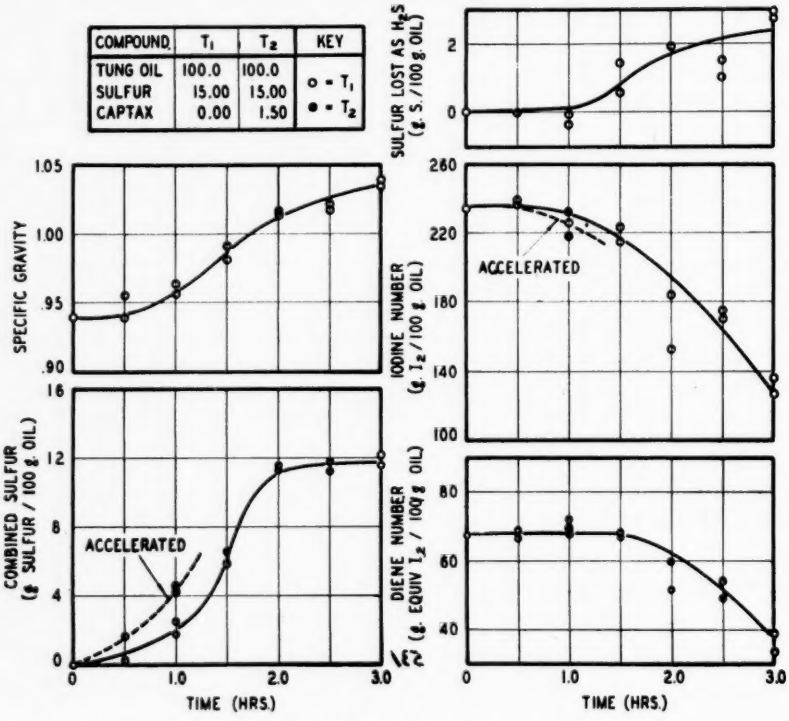


FIG. 2.—Vulcanization of tung oil.

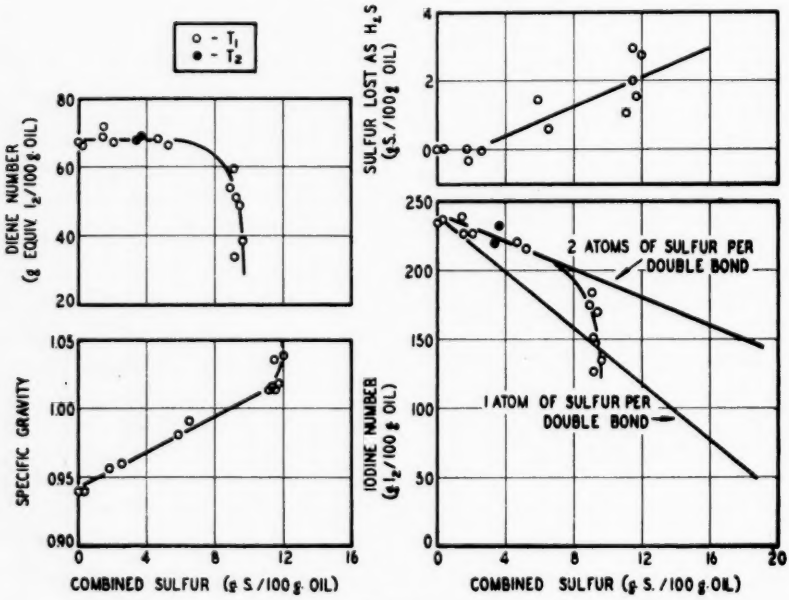

○ - T1
● - T2
DIENE NUMBER (g EQUIV I2/100 g OIL)
SULFUR LOST AS H2S (g S./100 g OIL)
SPECIFIC GRAVITY
IODINE NUMBER (g I2/100 g OIL)
2 ATOMS OF SULFUR PER DOUBLE BOND
1 ATOM OF SULFUR PER DOUBLE BOND
COMBINED SULFUR (g S./100 g OIL)
COMBINED SULFUR (g S./100 g OIL)

FIG. 3.

maleic anhydride (Diels and Alder), remains constant until practically all sulfur has combined. By considering the structure of eleostearic acid, it can be shown why the diene number can remain constant.

$$CH_3(CH_2)_3\underset{1}{CH}=\underset{2}{CH}-\underset{3}{CH}=\underset{4}{CH}-\underset{5}{CH}=\underset{6}{CH}(CH_2)_7COOH$$

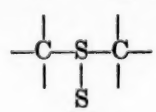
The condensation of maleic anhydride with a conjugated system requires only two of the double bonds. It is possible, therefore, to reduce the unsaturation of the acid chain by one double bond without altering the diene number. Two possibilities for this loss of unsaturation present themselves: a 1,2(5,6)- or a 1,6-addition of sulfur. The fact that the diene number remains constant while combined sulfur increases means that the net removal of one double bond from each acid chain renders the remaining two double bonds less reactive toward further combination with sulfur. In the case of a 1,2-addition, it would seem improbable that the 5,6-positions are inhibited; whereas in the event of a 1,6-addition, steric or other factors would tend to render the remaining two double bonds less reactive. Furthermore, conjugated systems of such a type generally react at their terminal carbon atoms. Therefore, it is assumed that addition of sulfur to eleostearic acid takes place at the 1,6-positions of the conjugated system.

The results presented in Figure 3 indicate furthermore that, in the early part of vulcanization, sulfur combines with tung oil at a ratio of two atoms of sulfur to each double bond. It is also shown that hydrogen sulfide is not liberated until after some of the sulfur has combined. Thus it seems that, in the early stages of vulcanization, combination of sulfur must take place with two atoms of sulfur saturating one double bond. This seems quite logical if consideration is given to the chemistry of sulfur. In its elementary state and under ordinary conditions, a sulfur molecule has eight atoms arranged in the form of a ring.[13] Before it can react, it must decompose into smaller "molecules"; for example in the following way:

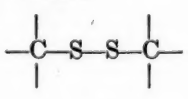
$$S_8 \rightarrow S_4 \rightarrow S_2 \rightarrow S_1{}^{14} \qquad \text{(I)}$$

It is believed that the elevated temperatures used in this investigation and the presence of the unsaturated organic substance, which is able to dissolve sulfur and act as acceptor, favor this decomposition. In the case of tung oil, owing to the high reactivity of the terminal carbon atoms of the conjugated systems, some sulfur can react in diatomic form before decomposing to the atomic state.

Combination of two atoms of sulfur for each double bond permits the visualization of the following two probable types of sulfur linkages:

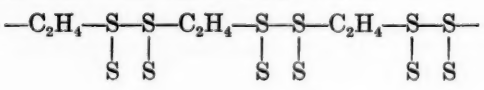


(a)

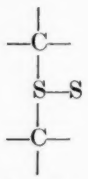


(b)

Qualitative tests[15] have failed so far to show the presence of disulfide linkages (formula b), although it must be admitted that such tests are inconclusive. Thiokol is reported to have the following structure:[15]



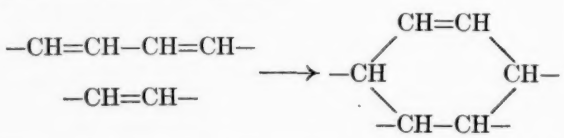
Owing to the weakness of the sulfur-sulfur bond, exactly 50 per cent of the sulfur in Thiokol can be removed by an alkali extraction. Therefore, if there are also some



linkages in factice, an alkali extraction should remove some sulfur. This was found experimentally to be true.

Presumably at a later stage of vulcanization there is also combination of sulfur in the monatomic state. At the same time, owing to the instability of the sulfur-sulfur bond in S—S linkages, some sulfur in this form decomposes to give a thioether linkage and hydrogen sulfide. Simultaneous occurrence of these two reactions would still make the ratio of atoms of sulfur combined to the number of double bonds lost about two.

The large drop in unsaturation and diene number after all sulfur has combined (Figure 3) is believed to be due to polymerization of the oil. This opinion is supported by the simultaneous increase in specific gravity. Studies on the polymerization of drying oils have shown that tung oil polymerizes according to the familiar Diels and Alder mechanism: [17]



In the present case, polymerization occurs presumably according to the same mechanism. If this is correct, there must be a loss of one diene number for every loss of two iodine numbers. This has been experimentally verified (Figure 4).

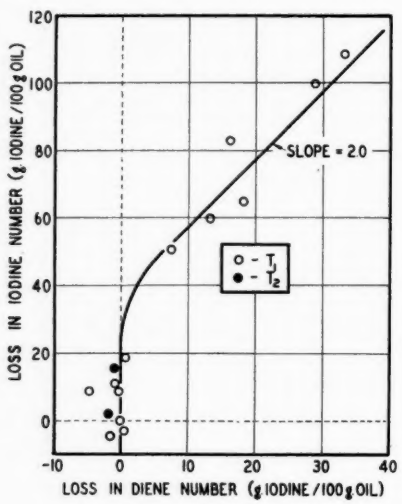


FIG. 4.

The formation of tung oil factice can be accelerated by the use of mercaptobenzothiazole.

Data on the vulcanization of linseed oil are presented in Figures 5 and 6. From Figure 6 it can be seen that, for simple linseed oil and sulfur mixtures, sulfur combines at a ratio of greater than one but less than two atoms of sulfur per double bond. This evidently cannot be accounted for by one simple reaction. As in the vulcanization of tung oil, hydrogen sulfide is liberated only after some of the sulfur has combined. Referring to reaction I, we can account for the ratio at which sulfur combines as a simultaneous addition of S_2 and S_1 to the double bonds of linseed oil. With the addition of zinc oxide, sulfur is shown to combine at a ratio of almost two atoms of sulfur for each double bond lost

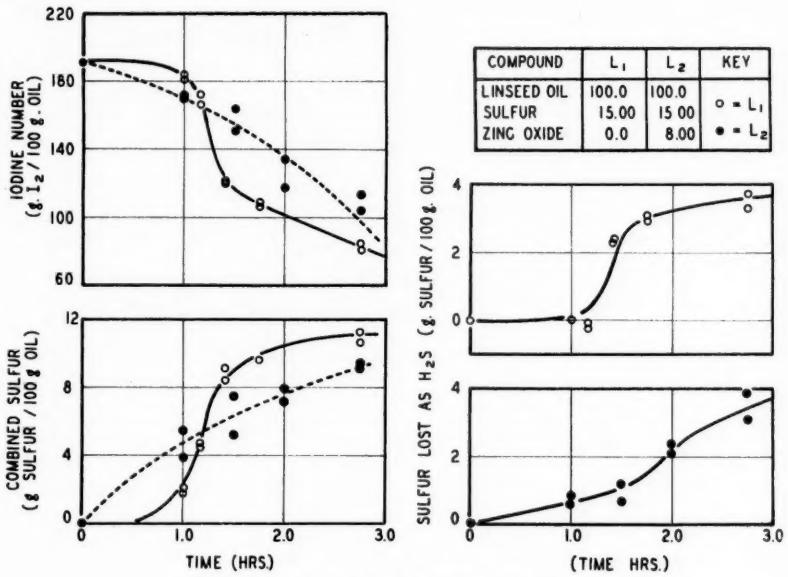

IODINE NUMBER (g. I2 / 100 g. OIL)
COMBINED SULFUR (g SULFUR / 100 g OIL)
TIME (HRS)
SULFUR LOST AS H2S (g. SULFUR / 100 g. OIL)
(TIME HRS.)
COMPOUND | L1 | L2 | KEY
LINSEED OIL | 100.0 | 100.0
SULFUR | 15.00 | 15.00
ZINC OXIDE | 0.0 | 8.00
○ = L1
● = L2

FIG. 5.—Data on the vulcanization of linseed oil.

(Figure 6). This can be explained by assuming that zinc oxide activates diatomic sulfur and accelerates its addition, so that, during the early part of vulcanization, a great deal more sulfur combines in the diatomic form than in the atomic state. It has been known for a long time that inorganic bases, such as zinc oxide, are able to activate sulfur and accelerate the vulcanization of rubber.[18] Liberation of hydrogen sulfide from both of the linseed oil compositions investigated is again attributed to the decomposition of

linkages. Toward the end of the vulcanization, the relatively large decrease of unsaturation, accompanied by only a small increase of combined sulfur, is be-

lieved to be the result of polymerization. According to recent studies on drying oils, isolated double bonds of the fat acids of linseed oil are isomerized by heat to conjugated systems, and are then polymerized according to a Diels and Alder mechanism.[17] It is believed that the same mechanism applies here.

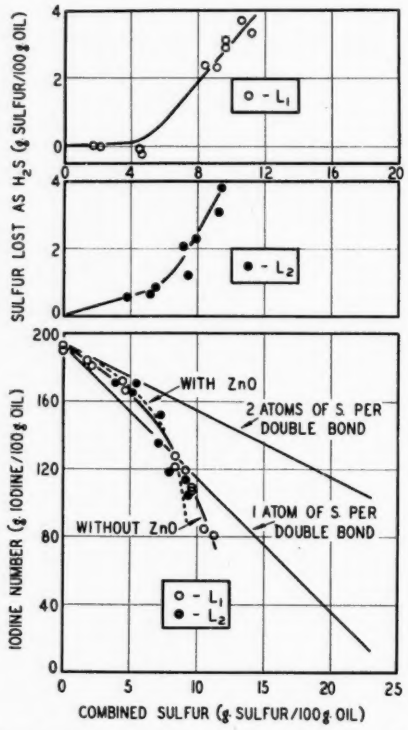

SULFUR LOST AS H_2S (g SULFUR/100 g OIL)
o - L_1
● - L_2
IODINE NUMBER (g IODINE/100 g OIL)
WITH ZnO
2 ATOMS OF S. PER DOUBLE BOND
1 ATOM OF S. PER DOUBLE BOND
WITHOUT ZnO
COMBINED SULFUR (g SULFUR/100 g OIL)

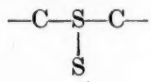
FIG. 6.—Data on the vulcanization of linseed oil.

THE VULCANIZATION OF RUBBER

Data on soft rubber vulcanization presented in previous papers[1] shows that the ratio of one atom of sulfur per double bond lost holds only for simple rubber-sulfur compounds. In all stocks containing organic accelerators or zinc oxide, combination of sulfur is generally in excess of one atom of sulfur to each double bond lost. These results can be explained if we assume that, in simple rubber-sulfur compounds, only S_1 is active enough to combine with the double bonds. Combination may occur either intermolecularly, forming thioether cross-linkages, or intramolecularly according to the scheme of Midgley, Henne, and Shepard.[19] In the presence of organic accelerators, or of inorganic bases like zinc oxide, diatomic sulfur also is activated. The relative predominance of the combination of diatomic or monatomic sulfur determines the observed ratio of atoms of sulfur combined per double bond lost.

Diatomic sulfur can combine with rubber in two ways, resulting in structures identical with those previously discussed in the case of factice formation. Again

no indication of disulfide linkages is available. Furthermore, disulfide linkages should be very unstable at the vulcanizing temperature. Therefore, a



structure seems most probable.

The formation of soft vulcanized rubber has been accounted for by sulfur cross-linkages between rubber molecules. On the other hand, the formation of hard rubber is believed to be due to intramolecular addition of sulfur, since ebonite is still noticeably thermoplastic. Soft rubber formation always precedes hard rubber formation. From the insolubility and the infusibility of soft rubber and the thermoplasticity of hard rubber, it becomes apparent that cross-linkages are formed mostly in the early part of vulcanization. After a certain number of cross-linkages has been formed, further combination of sulfur does not seem to produce more. This is an assumption that has to be accounted for. According to Boggs and Blake,[20] the terminal unsaturated groups are more reactive than those in the middle of the molecular chains. Thus, a reaction occurs there first. Therefore it can be assumed that cross-linking at the terminal double bonds is primarily responsible for the formation of soft rubber. Of all possibilities it is most probable that such cross-linking involves only one terminal double bond and any other double bond which happens to be in the nearest neighborhood. For a single rubber molecule, cross-linking therefore precedes intramolecular addition, owing to the higher reactivity of the terminal double bonds. In a mass of rubber molecules, both reactions occur simultaneously, since not all of the molecules react at the same time. Over a longer period of vulcanization, intramolecular addition of sulfur becomes increasingly predominant, while cross-linking ceases.

By using this concept, many other observations made during vulcanization can be explained.

Even if less than 1 per cent of sulfur is theoretically required for vulcanization,[21] we actually have to use more, because cross-linking is not the only reaction which takes place. Owing to the fact that organic accelerators or zinc oxide can activate S_2 and accelerate its cross-linking reaction, much less sulfur, a shorter time, and a lower temperature are required for accelerated stocks to reach optimum cure than for simple rubber-sulfur compounds. Since we must consider more than one type of sulfur combination, no simple relation can exist between the percentage of combined sulfur and the physical properties of the vulcanizate.

From the above discussion it follows that the vulcanization of simple rubber-sulfur compounds to ebonite should proceed continuously at a ratio of one atom of sulfur per double bond lost. Substitution should be negligible. Fisher and Schubert [22] have found experimentally that substitution is actually negligible in the vulcanization of rubber-sulfur stocks when theoretical proportions of sulfur are used. In the presence of accelerators or zinc oxide, the result should be different. Results on hard rubber vulcanization are given in Figures 7 and 8. From Figure 8 we can see that, in the presence of diphenylguanidine or zinc oxide, the initial ratio at which sulfur combines is about two atoms of sulfur per double bond. As vulcanization proceeds, the ratio decreases to approximately one atom of sulfur per double bond. During the early stage of vulcanization in the presence of such additional agents, cross-linking of activated S_2 involving the terminal double bonds takes place. Later, only intramolecular addition of atomic sulfur

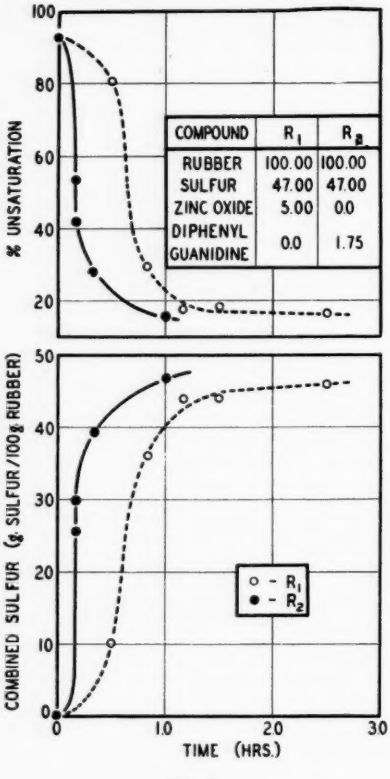

% UNSATURATION
COMPOUND | R1 | R2
RUBBER | 100.00 | 100.00
SULFUR | 47.00 | 47.00
ZINC OXIDE | 5.00 | 0.0
DIPHENYL GUANIDINE | 0.0 | 1.75
COMBINED SULFUR (g SULFUR/100g RUBBER)
TIME (HRS.)
○ - R1
● - R2

FIG. 7.

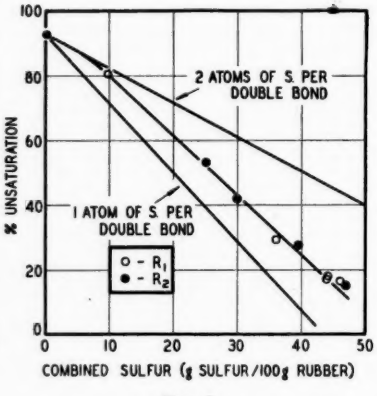
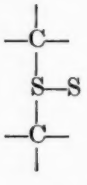


FIG. 8.

FIG. 7.—Results on hard rubber vulcanization.
FIG. 8.—Results on hard rubber vulcanization.

occurs, resulting in hard rubber. During vulcanization to ebonite, a small quantity of hydrogen sulfide is liberated. This is believed to be due to the decomposition of



linkages.

In the presence of addition agents, it has been noticed that, even after a coefficient of vulcanization of 46 has been reached, there still remains about 15 per cent of the original unsaturation (Figures 7 and 8). Thus it is possible to have a coefficient of vulcanization greater than 47 in accelerated compounds.

It has been found,[1] in the vulcanization of soft rubber, that prolonged heating after all sulfur has combined decreases the unsaturation. This was explained as the result of double bond polymerization of rubber hydrocarbon, giving four-carbon-atom rings. In the case of hard rubber vulcanization, prolonged heating after all sulfur has combined does not show this effect. This seems

logical because, with only a few free double bonds scattered in a mass of rubber chains, polymerization is improbable. Further evidence of polymerization is given by Curtis, McPherson, and Scott.[23] They found that with rubber with low coefficients of vulcanization, "prolonged heating, after the combination of rubber and sulfur is complete, increases the density." The possible criticism that cyclobutane is unstable, owing to the strain at the bonds, can be negated by the fact that substituted cyclobutanes have been found to show remarkable stability.[24]

CONCLUSIONS

From the preceding discussion the following conclusions may be drawn:

A. Vulcanization with Sulfur in General

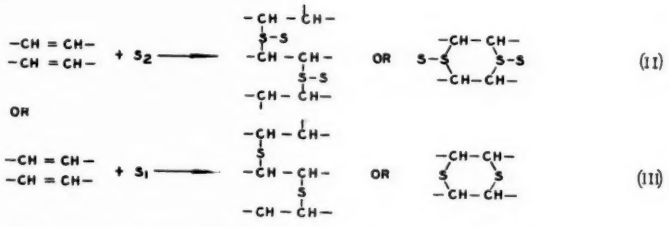
1. Vulcanization with sulfur is fundamentally a chemical change involving activated sulfur and organic double bonds.
2. Sulfur must decompose from S_8 (in the form of an eight-membered ring) to smaller molecular units, perhaps to S_2 and S_1, before it can be activated and react.
3. The ratio of atoms of sulfur combined to the number of double bonds lost is not restricted to one atom of sulfur for each double bond, but may have other values, which depend on the conditions and the reactions involved.

B. Factice Formation

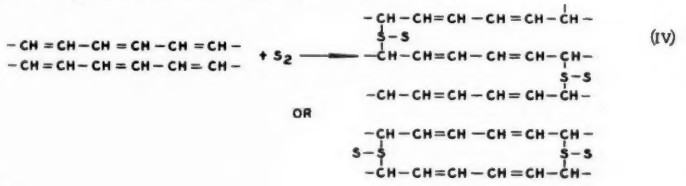
1. The rate of reaction of sulfur with tung and linseed oils is greatly influenced by small proportions of such agents as zinc oxide and mercaptobenzothiazole.
2. Combination of sulfur with the conjugated double bonds of the eleostearic acid in tung oil takes place at the terminal carbon atoms of the conjugated system, giving a typical 1,6-addition.
3. The following possible chemical reactions explain adequately the process of factice formation from tung and lineseed oil. Under different conditions different reactions predominate.

(*a*) *Addition:*

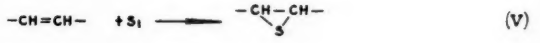
Intermolecular:



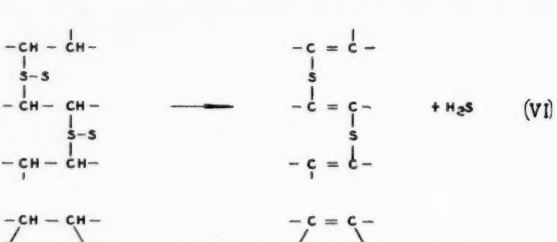
In the case of conjugated double bonds (eleostearic acid):



Intramolecular:



(*b*) *Dehydrogenation:*



(VI)

(*c*) *Polymerization:*

(VII)

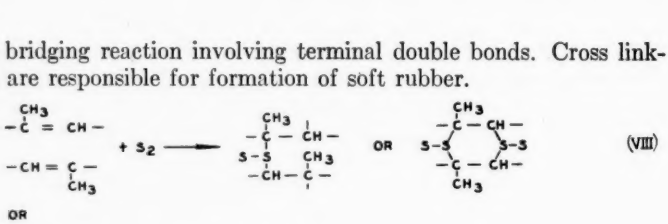
C. Rubber Vulcanization

1. The coefficient of vulcanization in the presence of accelerators or zinc oxide can exceed the value of 46.

2. The results obtained from studies on rubber vulcanization at elevated temperatures can be conveniently explained by assuming the following reactions:

(*a*) *Addition:*

Intermolecular bridging reaction involving terminal double bonds. Cross linkages thus formed are responsible for formation of soft rubber.

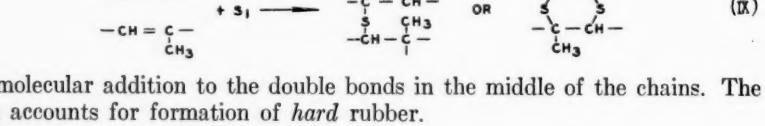


(VIII)

OR

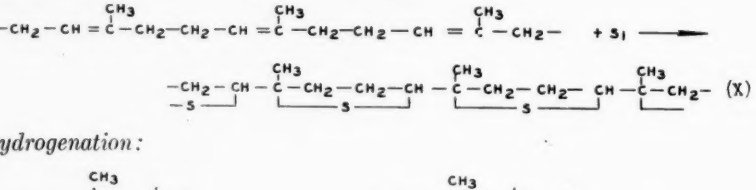
(IX)

Intramolecular addition to the double bonds in the middle of the chains. The reaction accounts for formation of *hard* rubber.



(X)

(*b*) *Dehydrogenation:*



(XI)

(c) *Double-bond polymerization:*

Prolonged heating after all sulfur has combined in soft rubber vulcanization induces polymerization:

(XII)

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[11] The procedure is best illustrated by the following specific example: A 0.1-0.15-gram sample is weighed into a carefully cleaned and dried Erlenmeyer flask with a ground-glass joint. Pure carbon tetrachloride or chloroform is then added to dissolve the sample. In the case of pure tung oil or not highly vulcanized samples, whirling of the flask for a short time will facilitate solution. But in the case of solid factice, it is necessary to heat the contents under a reflux condenser, in order to swell and disintegrate the solids. Owing to the low boiling point of the solvent, heating does not cause any polymerization, as time of refluxing has practically no effect on the final iodine number. The solution, which may be colloidal, is allowed to cool to room temperature. Enough iodine bromide reagent is added to assure the proper excess (80 per cent). After the content has been allowed to react for 2 hours at room temperature, 15 cc. of water is added. The mixture is then titrated for iodine against a standard sodium thiosulfate solution, using starch as indicator. Blanks must be run simultaneously. From the titration of the blank and the titration of the sample, the iodine number can be calculated on the basis of the iodine equivalent of the thiosulfate solution.
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EVALUATION OF THE BUFFER CAPACITY OF CRUDE RUBBERS *

E. B. NEWTON [1] and E. A. WILLSON [1]

MALAYAN RESEARCH LABORATORIES, THE B. F. GOODRICH COMPANY, KUALA LUMPUR, FEDERATED MALAY STATES

The hypothesis was advanced in the preceding paper that an important factor in determining the rate of cure of rubber is the acid-base equilibrium developed during vulcanization and that such an equilibrium is determined to a large extent by the nature and quantity of the latex serum substances remaining in the crude rubber mass. In effect, this serum material was regarded as a buffer substance.

If this were true, it follows that differences in the buffer capacities of various crude rubbers should be demonstrable and, in the following discussion, two sets of experiments designed with this object in view are described.

EXPERIMENTAL

In the first series, two rubbers were chosen—first-latex crepe and a commercial latex-sprayed (made by spray-drying ammoniated latex)—showing widely different rates of cure in a rubber-sulfur stock. The rubbers were compounded in base recipe D (100 rubber-10 sulfur), and graded quantities of phosphoric acid were introduced into these batches (Table I). The acid was mixed with the sulfur powder, which was then worked into the rubber running as a rolling bank on the mixing mill. The lower concentrations of acid (up to 8 grams H_3PO_4 per 650 grams of rubber) were added as aqueous solutions, with the total liquid volume kept at 10 cc. or less. Above 8 grams H_3PO_4 per 650 grams of rubber, the acid was added as 85 per cent sirupy phosphoric acid.

The results of the curing tests are shown in Figure 1; the times of cure to

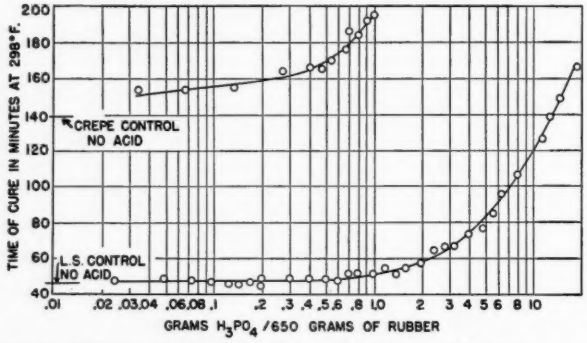

FIG. 1.—Influence of phosphoric acid on rate of cure of first latex crepe and latex-sprayed rubbers in basic stock D.

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 34, No. 3, pages 378-382, March 1942. This paper was presented before the Division of Rubber Chemistry at the 102nd Meeting of the American Chemical Society at Atlantic City, N. J., September 12, 1941.

TABLE I

EFFECT OF PHOSPHORIC ACID ADDITIONS ON CURE OF BATCHES OF RUBBER D[a]

SPRAYED-LATEX RUBBER															
Recipe No.	D	4DR	4DS	4DT	4DU	4DV	4DW	4DX	4DY	4DZ	—	—	—	—	—
H_3PO_4/batch	—	0.024	0.048	0.072	0.096	0.125	0.144	0.168	0.192	0.198	—	—	—	—	—
Time of cure [b]	49	48	49	48	47	46	46	47	45	49	—	—	—	—	—
Recipe No.	5DA	5DB	5DC	5DD	5DE	5DF	5DG	5DH	5DI	5DJ	5DK	—	—	—	—
H_3PO_4/batch	0.297	0.396	0.495	0.594	0.693	0.792	0.990	1.188	1.386	1.584	1.98	—	—	—	—
Time of cure [b]	49	49	49	48	52	52	52	55	52	55	58	—	—	—	—
Recipe No.	5DL	5DM	5DN	5DO	5DR	5DS	5DT	5DU	6DF	6DG	6DH	6DI	—	—	—
H_3PO_4/batch	2.376	2.772	3.168	3.960	4.752	5.544	6.336	7.920	11.10	12.95	14.80	18.50	—	—	—
Time of cure [b]	65	67	67	74	77	85	93	107	127	139	149	167	—	—	—
CREPE RUBBER															
Recipe No.	D	5DV	5DW	5DX	5DY	5DB	6DA	6DB	6DC	5DE	5DF	6DJ	5DG		
H_3PO_4/batch	—	0.033	0.066	0.132	0.264	0.396	0.462	0.528	0.660	0.693	0.792	0.891	0.990		
Time of cure [b]	139	153	153	155	164	166	165	170	176	186	184	192	195		

[a] Press-cured at 298° F in aluminum foil.
[b] To reach a modulus of 2100 lbs. per sq. in. at 800 per cent elongation.

reach a modulus of 2100 pounds per square inch at 800 per cent elongation are plotted against the quantities of H_3PO_4 per 650 grams of rubber. The addition of a given quantity of acid has far less effect on slowing the cure L. S. (latex-sprayed) than of crepe; moreover, for any given range of acid additions, the slope of the curve is less for L. S. rubber than for crepe. The L. S. rubber acts as though it were more strongly buffered than does the crepe rubber[2].

The other series of experiments amounted to an attempt to determine the acid-neutralizing power of the serum substances in different crude rubbers. With due regard to whatever limitations may have been imposed by diffusion or by reaction of acid with rubber hydrocarbon, the method employed gave an electrometric titration of the serum substances.

The procedure employed was as follows. The dry crude rubber was passed four or five times through close-set mill rolls to form a thin crepe sheet about $\frac{1}{32}$ inch thick. A 2-gram sample in rectangular form was cut out and rolled spirally but loosely into a cylinder without any dusting or parting layer. Generally eight samples (2 grams each) were prepared from each crude rubber

TABLE II

pH OF AQUEOUS CONTENTS OF VARIOUS RUBBERS AFTER 17-HOUR IMMERSION AT 90° C

	Rubber number						
Standard HCl used	974[a]	936[b]	537[c]	797[d]	965[e]	906[f]	Control
Distd. water only (10 cc.)	8.00	8.70	6.55	6.90	6.21	4.55	5.85
1 cc. 0.001 *N*[g]	8.03	8.66	6.54	7.02	5.66	4.32	4.45
2 cc. 0.001 *N*[g]	8.10	8.64	6.54	6.78	4.64	4.07	3.94
3 cc. 0.001 *N*[g]	8.07	8.69	6.52	6.58	4.22	3.88	3.73
5 cc. 0.001 *N*[g]	8.11	8.59	6.50	5.94	3.74	3.65	3.50
10 cc. 0.001 *N*	8.06	8.25	6.45	4.25	3.37	3.35	3.20
10 cc. 0.002 *N*	7.99	7.45	6.29	3.15	2.94	2.95	2.85
10 cc. 0.005 *N*	7.83	3.93	5.89	2.56	2.50	2.50	2.44

[a] Fraction skimmed from centrifugal concentration of latex, containing about 0.4 g. of NH_3 per 100 g. of skim coagulated by addition of 0.5% by weight of $CaCl_2$ and by introducing steam to heat the skim directly to 80° C. Rubber clot creped and air-dried at 130° F.
[b] Fraction skimmed (as rubber 974), aerated to reduce NH_3, then allowed to coagulate spontaneously by fermentation; clot creped and air-dried at 130° F.
[c] Commercial L. S. rubber, by spray-drying ammoniated latex.
[d] Air-dried (at 130° F) unsmoked sheet coagulated with acetic acid at 15% dry rubber content.
[e] Specially washed unsmoked sheet showing low water absorption.
[f] Unsmoked sheet coagulated with alum at 15% dry rubber content.
[g] Diluted to 10 cc.

tested. They were placed in Pyrex-glass test-tubes (soft glass must be avoided) and covered with 10 cc. of hydrochloric acid solution, as listed in Table II and plotted in Figure 2. A short length of Pyrex rod bent as a V or L was dropped onto the rubber to keep it submerged. A control series of solutions without rubber but with the Pyrex weights was always run. The tubes were closed with corks wrapped in tin foil (glass stoppers would have been preferable). The solutions were not in contact with the metal. The tubes were heated overnight (16 hours) in a forced-draft air oven at 90° C, then removed, shaken to stir contents, and replaced in the oven for another hour. The tubes were then taken from the oven, cooled in water, and shaken to collect water droplets on the inside of the tube, and the pH of each solution was determined with a glass electrode.

Table III contains data (see also Figure 2) on a series of rubbers prepared from different latices by widely varying methods.

Titration of the serum substances in several other rubbers was carried out. Eight samples of RSS No. 1 from the standard production of different Malayan estates were chosen as representing a fairly wide variation in rate of cure, both in the mercaptobenzothiazole and rubber-sulfur stocks. Tables IV and V give

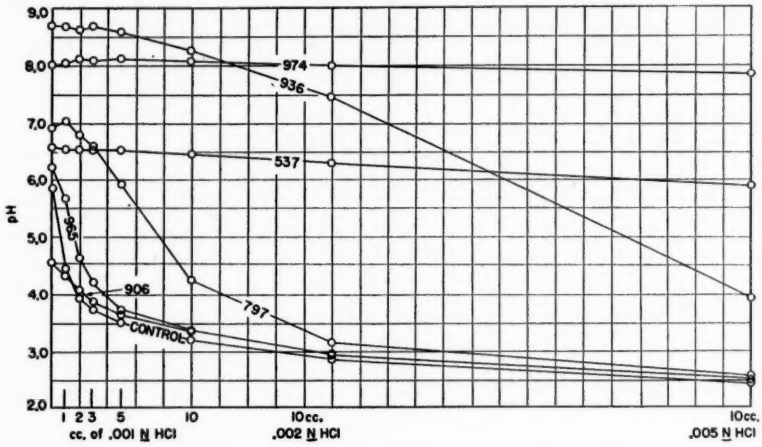

FIG. 2.—Titration of serum material in rubbers prepared by various means.

Rubber No.	Treatment	Tensile strength of recipe AM,[a] lbs. per sq. in.	Time of cure [b] of recipe D (min.)
974	Skim	2620	<15
936	Skim	3660	48
537	L. S.	1850	45
797	Sheet	1650	95
965	Thin sheet rubber (specially washed)	500	134
906	Alum-coagulated	80	171

[a] 40-minute cure at 260° F, 700% elongation.
[b] Time to reach 2100 lb. per sq. in. at 800% elongation (298° F).

data on rubbers 940 to 947, and in Figure 3 the titration results are plotted. The enlarged pH scale in Figure 3 should not be regarded as indicating an accuracy greater than that in Figure 2, but merely to render the curves more legible. A correlation between the titration data of the rubbers and their rates of cure in both the mercaptobenzothiazole and rubber-sulfur stocks is indicated in Figure 3.

DISCUSSION

The curves of Figure 2 line up roughly in accordance with the rates of cure in both the mercaptobenzothiazole and rubber-sulfur mixes; the rubbers having the greatest buffer capacity at the higher pH values are fastest, while alum rubber 906, whose curve actually crosses that of the control, is slowest. Particularly interesting is the fermented skim rubber 936, which in the curing tests was by far the fastest in the rubber-sulfur mix, but which proved slower than skim rubber 974 and L. S. rubber 537 in the mercaptobenzothiazole stock. This crossing over is indicated by the titration curves if the assumption is made that the concentration of acidic materials (for example, hydrogen sulfide[3]) is greater in the rubber-sulfur stock during cure than in the mercaptobenzothiazole stock. Inasmuch as the titration data indicate that the buffer capacity of rubber 936 is low relative to that of rubbers 974 and 537, the higher concentration (assumed) of hydrogen sulfide in the rubber-sulfur stock during cure would be expected to shift the acid-base equilibrium to some lower value, possibly lower than the equilibrium in the other two rubbers. (The presence of zinc oxide in the

TABLE III

TENSILE STRENGTHS OF ACID-TREATED RUBBERS PREPARED BY WIDELY DIFFERENT METHODS

A. C. S. CAPTAX STOCK, PRESS-CURED AT 260° F (RECIPE AM)

Cure (min.)	600%	700%	At break	600%	700%	At break
	Rubber 974			Rubber 936		
20	1525	2270	2680 (747%)	—	—	—
30	—	—	—	1700	3340	3720 (725%)
40	1815	2620	2930 (730%)	—	3660[a]	—
45	—	—	—	2260	3810	3810 (700%)
60	1940	2900	3340 (747%)	2680	—	3760 (675%)
75	—	—	—	3090	—	3450 (627%)
80	2020	3000	3520 (760%)	—	—	—
90	—	—	—	2910	—	3050 (615%)
100	2050	3090	3500 (740%)	—	—	—
120	2280	3280	3685 (745%)	2630	—	3060 (630%)
	Rubber 537			Rubber 797		
20	750	1500	2230 (773%)	—	—	—
30	—	—	—	640	1420	3100 (837%)
40	1070	2040	2630 (750%)	—	1650[a]	—
45	—	—	—	820	1760	3070 (797%)
60	1150	2300	2700 (733%)	910	2000	3220 (790%)
75	—	—	—	880	1910	3330 (807%)
80	1180	2290	2840 (747%)	—	—	—
90	—	—	—	950	2050	3480 (795%)
100	1290	2420	2650 (720%)	—	—	—
120	1320	2410	2700 (730%)	930	2040	3390 (810%)
	Rubber 965			Rubber 906		
20	150	275	380 (787%)[b]	—	—	No cure
40	230	500	1020 (825%)[b]	50	80	400 (857%)[b]
60	330	620	1260 (800%)[b]	160	320	960 (887%)[b]
80	350	620	1220 (780%)[b]	220	390	1450 (897%)
100	390	740	1730 (840%)	260	490	1680 (887%)
120	400	740	1760 (837%)	270	550	1710 (863%)

RUBBER-SULFUR STOCK, PRESS-CURED AT 298° F (RECIPE D)

Cure (min.)	700%	800%	At break	700%	800%	At break
	Rubber 974			Rubber 936		
15	2250	3460	3560 (807%)	—	—	—
30	2680	—	2940 (720%)	550	1160	2310 (890%)
45	—	—	1525 (490%)	—	—	—
60	—	—	1225 (393%)	1570	2750	2750 (800%)
90	—	—	1170 (345%)	—	—	430 (410%)
120	—	—	1200 (360%)	—	—	370 (360%)
150	—	—	—	—	—	350 (347%)
	Time of cure		15 min.			48 min.
	Rubber 537			Rubber 797		
15	220	325	540 (900%)[b]	—	—	—
30	530	1050	2500 (955%)	160	290	540 (917%)[b]
45	910	1790	2910 (890%)	—	—	—
60	1630	2890	3180 (825%)	375	790	2250 (955%)
90	—	—	1560 (570%)	890	1920	2950 (870%)
120	—	—	640 (387%)	1770	—	2900 (780%)
150	—	—	—	—	—	730 (505%)
	Time of cure		49 min.			95 min.
	Rubber 965			Rubber 906		
60	300	510	880 (880%)[b]	160	280	900 (1007%)
90	500	975	1520 (857%)[b]	300	540	1450 (967%)
120	900	1860	2360 (845%)	450	950	2050 (933%)
150	1320	2380	2930 (830%)	730	1575	2410 (877%)
180	1890	—	2930 (770%)	1160	2270	2690 (830%)
210	—	—	—	1560	—	2680 (790%)
	Time of cure		134 min.			171 min.

[a] Interpolated from family of stress-strain curves.
[b] Jaw break.

TABLE IV

pH OF AQUEOUS CONTENTS OF RUBBERS 940 TO 947 [a] AFTER 17-HOUR IMMERSION AT 90° C

Standard HCl used	Rubber number								
	940	941	942	943	944	945	946	947	Control
Distd. water only (10 cc.)	5.36	6.30	6.03	5.20	4.45	4.29	6.36	4.30	6.35
1 cc. 0.001 *N* [b]	5.02	6.05	5.96	4.93	4.25	4.10	6.22	4.15	4.42
2 cc. 0.001 *N* [b]	4.90	5.79	5.67	4.60	4.13	4.14	6.05	4.03	3.90
3 cc. 0.001 *N* [b]	4.58	5.62	5.55	4.42	4.03	3.85	5.87	3.85	3.71
5 cc. 0.001 *N* [b]	4.20	5.04	4.96	4.05	3.85	3.67	5.60	3.65	3.46
10 cc. 0.001 *N*	3.70	4.15	4.20	3.62	3.48	3.38	4.84	3.35	3.23
10 cc. 0.002 *N*	3.05	3.15	3.23	3.06	3.00	2.97	3.50	2.92	2.85
10 cc. 0.005 *N*	2.50	2.56	2.57	2.52	2.50	2.50	2.64	2.50	2.45

[a] These rubbers were all standard ribbed smoked sheet No. 1, chosen from the output of a number of estates to show wide variation in rate of cure.
[b] Diluted to 10 cc.

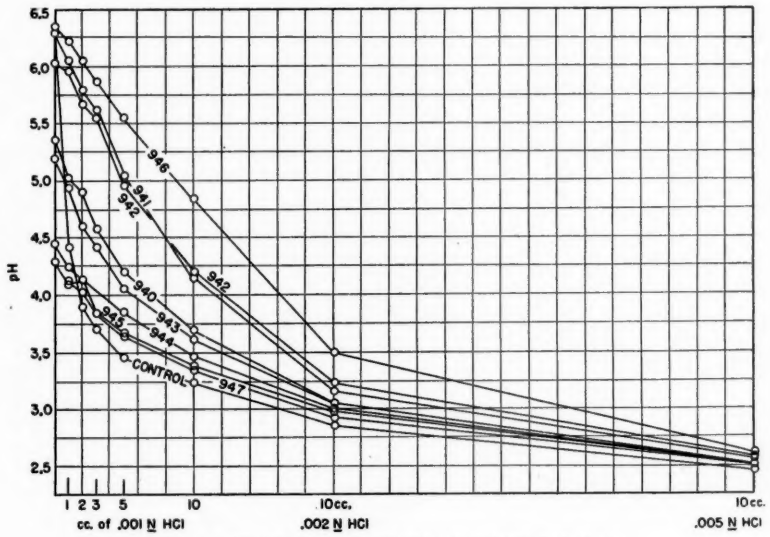

FIG. 3.—Titration of serum material in rubbers 940 to 947.

Rubber No.	Tensile of recipe AM,[a] lbs. per sq. in.	Time of cure [b] of recipe D, (min.)
946	2110	104
941	1630	103
942	1490	117
940	1240	144
943	1200	141
944	860	152
945	680	179
947	450	187

[a] 40-minute cure at 260° F, 700% elongation.
[b] Time to reach 2100 lb. per sq. in. at 800% elongation (298° F).

mercaptobenzothiazole stock may possibly assist, but the action of zinc oxide in a stock is regarded as something other than assisting the acid-base equilibrium toward alkalinity. There are also further factors in these tests which presumably act to lower concentration of hydrogen sulfide; namely, the quantity of sulfur on the rubber is less in the mercaptobenzothiazole mix and the temperature of cure is lower.)

This measurable titration of the serum substances in rubber is regarded as indicative of a means of determining a major factor in the rate of cure of that

TABLE V

TENSILE STRENGTHS OF ACID-TREATED RUBBERS 940 TO 947

MERCAPTOBENZOTHIAZOLE STOCK, PRESS-CURED AT 260° F (RECIPE AM)

Cure (min.)	600%	700%	At break	600%	700%	At break	600%	700%	At break	600%	700%	At break
	Rubber 940			Rubber 941			Rubber 942			Rubber 943		
30	450	1140	2260 (837%)	650	1340	2490 (823%)	560	1160	2310 (837%)	380	780	1900 (870%)
40	580	1240	2470 (817%)	760	1630	2660 (810%)	740	1490	2420 (797%)	580	1200	8300 (830%)
60	800	1670	2700 (787%)	1050	2080	2850 (767%)	910	1870	2780 (783%)	720	1450	2290 (780%)
75	850	1800	2690 (780%)	1120	2150	3090 (780%)	960	1970	2700 (773%)	750	1520	2490 (790%)
90	860	1810	2860 (783%)	1120	2250	2850 (775%)	1000	2050	2830 (770%)	830	1640	2580 (793%)
120	950	1970	2900 (780%)	1220	2330	3000 (753%)	1100	2110	2610 (750%)	950	1750	2590 (785%)
	Rubber 944			Rubber 945			Rubber 946			Rubber 947		
30	310	600	1360 (870%)	220	420	1250 (910%)	900	1760	2850 (790%)	160	280	1040 (914%)
40	400	860	1730 (835%)	340	680	1650 (874%)	1060	2110	2960 (774%)	250	450	1500 (900%)
60	550	1140	1990 (804%)	480	960	2010 (835%)	1240	2340	3250 (764%)	340	720	1960 (884%)
75	700	1350	2120 (800%)	560	1150	2060 (810%)	1230	2370	3180 (760%)	400	790	2160 (865%)
90	690	1430	2300 (790%)	550	1160	2350 (834%)	1310	2620	3350 (747%)	410	850	2160 (854%)
120	740	1400	2350 (794%)	690	1340	2500 (814%)	1280	2570	3270 (755%)	490	990	2360 (844%)

RUBBER-SULFUR STOCK, PRESS-CURED AT 298° F (RECIPE D)

Cure (min.)	700%	800%	At break	700%	800%	At break	700%	800%	At break	700%	800%	At break
	Rubber 940			Rubber 941			Rubber 942			Rubber 943		
60	190	300	1180 (1020%)	390	725	1980 (950%)	340	540	1550 (990%)	230	360	1150 (1000%)
90	340	680	1910 (953%)	800	1580	2760 (900%)	600	1175	2200 (900%)	370	770	1770 (947%)
120	670	1410	2500 (902%)	1650	2920	3000 (810%)	1100	2225	2950 (860%)	740	2390	2390 (895%)
150	1310	2550	2730 (810%)	—	—	670 (467%)	—	—	1710 (677%)	1360	2510	2960 (830%)
180	—	—	1360 (645%)	—	—	420 (367%)	—	—	500 (410%)	—	—	1520 (663%)
Time of cure			144 min.			103 min.			117 min.			141 min.
	Rubber 944			Rubber 945			Rubber 946			Rubber 947		
60	250	390	840 (935%)	170	280	550 (925%)[a]	400	775	2050 (985%)	140	210	510 (973%)[a]
90	420	710	1600 (940%)	280	430	780 (870%)[a]	830	1560	2680 (890%)	230	410	1120 (960%)[a]
120	670	1260	2100 (890%)	450	880	1950 (920%)	1620	2900	3210 (825%)	360	690	1520 (920%)[a]
150	1050	2075	2660 (857%)	740	1460	2390 (880%)	—	—	510 (440%)	570	1190	2360 (905%)
180	1560	—	2660 (787%)	1080	2130	2670 (840%)	—	—	500 (400%)	890	1910	2780 (870%)
210	—	—	—	2020	—	2360 (730%)	—	—	—	1580	—	2380 (777%)
Time of cure			152 min.			179 min.			104 min.			187 min.

[a] Jaw break.

rubber. But attention may be called to the fact that it is possible to alter the rate of cure of a rubber without measurably changing the titration of the serum substances by the technique described. This can be done by introducing small quantities of a surface-active substance into latex before coagulation or, better, by milling some of the substance into dry sheet. For example, by milling 0.1 to 0.5 per cent of Aquarex-D (a sulfated alcohol) into various samples of rubber, their rates of cure were retarded, while the serum titration was not measurably altered[5]. Although the data presented in the tables do not preclude the action of such a factor arising from possible surface activity of some part of the serum substances or ingredients derived from the smoke in the case of commercial ribbed sheet, it is at present thought to be of lesser importance in an untreated crude rubber than the acid-base equilibrium referred to; hence by control of this titration value during preparation of the rubber, more uniform-curing commercial grades might be obtained.

If the hypothesis here advanced is essentially correct, the suggestion arises that the smoking of experimental sheet rubber prepared for vulcanization tests should be avoided, unless the effect of smoking itself is under test, since the control of smoking conditions, sometimes including the source of the wood used for firing, as generally practiced cannot be regarded as uniform. This lack of uniformity was shown in a striking way by Hastings and Rhodes[4]; by smoking identical wet sheet in different smoke houses, they were able to induce nearly as much variation in cure (particularly in the rubber-sulfur stock) as various tapping systems and seasonal variation showed over a period of months. This suggestion should be construed as applying only to the preparation of experimental rubbers. The practice of smoking in the preparation of estate sheet meets in a fairly satisfactory way a real problem in tropical climates—namely, inhibition of mould growth on sheet rubber during storage. There is time enough to devise a more satisfactory substitute to meet this requirement while the preparation of uniform curing plantation sheet in commercial quantities is under way.

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[4] Hastings and Rhodes, *Ind. Eng. Chem.* **31**, 1459, Table VI (1939).
[5] An example of the opposite type is thought to be the favorable action of metallic soaps, such as zinc stearate, in accelerated stocks. It is possible that these soaps are surface-active agents, which in some way favor, just as Aquarex-D retards, the vulcanization reaction. (An aqueous solution of Aquarex-D at room temperature is essentially neutral and, after boiling, is slightly alkaline, about pH 7.5.)

CURING RATE OF RUBBER

EFFECT OF PHOSPHATE BUFFER MIXTURES ON THE RATE OF CURE OF CREPE RUBBER *

E. B. NEWTON [1]

MALAYAN RESEARCH LABORATORIES, THE B. F. GOODRICH COMPANY, KUALA LUMPUR, FEDERATED MALAY STATES

The phenomenon of variability in the rate of vulcanization of crude rubber by sulfur and heat has been studied by rubber technologists for more than forty years. Whether early workers recognized differences in any particular commercial grade is difficult to say, as a result both of the lack of discriminating tests and of the secrecy which was formerly maintained in the industry. However, three developments, all coming near the beginning of this century, combined to make workers more aware of any differences which might exist: (1) Weber's work on the chemistry of rubber, which led to the first theory of cure[14] and to the idea of the sulfur coefficient of vulcanization[15]; (2) the wider availability and use of standardized tensile testing machines, although earlier but limited use of such machines was known[16]; and finally, (3) the rise of the plantation industry in the Middle East. The first two of these developments supplied methods of sufficient accuracy to detect differences other than by the empirical comparisons of hand tests. The third gave rise to many investigations designed to ascertain differences between the newer plantation and the standard Para grades.

All the early work on variability appears to have been done in consuming countries, and some of it was of primary importance. For example, Weber and Glidden[6] discovered in 1903 or 1904 the activating effect of oleic acid on litharge stocks which were compounded with rubber deficient in natural fat acids; Oenslager[9] in 1906, by vulcanization in the presence of aniline and, later, thiocarbanilide, was able to produce good physical properties in solvent-extracted rubbers, an observation which became the basis of a tremendous advance in rubber technology in consuming countries. But with the increase in planted acreage of *Hevea* rubber in the East shortly after, systematic investigations were undertaken by workers in that region to establish plantation rubber as equivalent in quality to Para on a scientific basis. This early work was both successful and comprehensive. Though many workers contributed, the extent of the field covered is shown in the summaries of the classic works of Eaton and coworkers[4], de Vries[12], and Khitby[16]. More recently, Hastings and Rhodes[7] and Sackett[10] extended the research on variability.

Variability in rate of vulcanization can arise from the composition of the latex as it comes from the tree, as well as from the operations employed to convert it into crude rubber. Whitby and de Vries noted that the higher rates of cure are associated with those rubbers which contain the higher quantity of serum substances, but just what portion of the serum solids, aside from the fat acids and

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from the nitrogen-containing products of putrefaction which appear to be true accelerators[3], are responsible for this relation has never been definitely stated.

De Vries[11] was once concerned over the possible effect of adding sodium bisulfite to latex as an inhibitor of oxidase action in the manufacture of crepe. In those days acetic acid was generally used as the latex coagulant and, since this combination might be expected to give rise to sodium acetate in the rubber, he tried the addition of this compound directly to latex before coagulation. Rubber thus prepared cured somewhat faster in a rubber-sulfur stock. He then soaked freshly machined sheets in a solution of sodium acetate and obtained a greater effect. Morton[8] added crystalline sodium acetate directly to rubber on the mixing mill, and obtained excellent activation in accelerated stocks.

Several years ago in the course of work on vulcanization, the use of sodium acetate as an activator was repeated. It was compounded (Table I) both in a rubber-sulfur stock and in the mercaptobenzothiazole test recipe of the Crude Rubber Committee of The American Chemical Society. First latex crepe, a slow-curing type, was used in one case, and a fast whole sprayed latex rubber in the other (Table II). The crepe was made as follows: Field latex was diluted to 15 per cent dry rubber content with tap water and coagulated by addition of

TABLE I

RECIPES FOR STOCK WITH SODIUM ACETATE AS ACTIVATOR

	Rubber-sulfur-type		Mercaptobenzothiazole type		
Recipe No.	D	6DK	AM	8AZ	9AE
Rubber	100	100	100	100	100
Sulfur	10	10	3.5	3.5	3.5
Zinc oxide	—	—	6	6	6
Stearic acid	—	—	0.5	0.5	0.5
Mercaptobenzothiazole	—	—	0.5	0.5	—
$NaC_2H_3O_2.3H_2O$	—	1.0	—	1.0	1.0

2 per cent acetic acid to pH 4.8 ± 0.1, determined by a glass electrode; the coagulum was creped the following day under a water spray, rolled thin (total of fifty passes), and dried in air at 50° C. The whole rubber was a commercial grade (called L. S. hereafter) made by spray-drying ammoniated latex.

The testing procedure was as follows: Batches of 650 grams of rubber were mixed on a 6×12 inch mill (gear ratio 1:1.4) and sheeted off (not calendered) to approximate mould size. They were press-cured the following day in chromium-plated moulds (unless otherwise stated), $6 \times 8 \times 0.1$ inch, without the use of any mould wash or other parting layer. Stress-strain data were obtained on the day following cure in $1 \times \frac{1}{4}$ inch dumbbell test-strips on a standard Scott autographic tensile machine (jaw separation 20 inches per minute), using two observers. The room temperature during mixing and testing was 28-30° C; the average relative humidity was 75 per cent.

Table II shows that the whole-rubber cures much faster than does the crepe in both the rubber-sulfur and the mercaptobenzothiazole stocks, a well known fact. In recipe 9AE, which contains no organic accelerator and insufficient sulfur for vulcanization in the absence of accelerator, sodium acetate is incapable of performing the functions of such an accelerator as mercaptobenzothiazole; but in both the rubber-sulfur and the mercaptobenzothiazole stocks, sodium acetate speeds up vulcanization, whether whole latex rubber or crepe is used, but especially the latter.

Table II

Effect of Sodium Acetate on Tensile Strength of Rubber (Pounds per Square Inch)

Rubber-sulfur type							Captax type									
Cure at 298° F (min.)	Recipe D 700%	Recipe D 800%	Recipe D At break	Recipe 6DK 700%	Recipe 6DK 800%	Recipe 6DK At break	Cure at 260° F (min.)	Recipe AM 600%	Recipe AM 700%	Recipe AM At break	Recipe 8AZ 600%	Recipe 8AZ 700%	Recipe 8AZ At break	Recipe 9AE 600%	Recipe 9AE 700%	Recipe 9AE At break
WITH FIRST LATEX CREPE RUBBER																
30	50	100	300 (1100%)	260	460	930 (910%)	20	150	340	1250 (940%)	640	1290	2400 (807%)	—	—	—
60	200	320	710 (913%)	700	1440	2350 (890%)	40	360	760	1980 (847%)	850	1770	2860 (790%)	—	—	—
90	360	760	1860 (937%)	1580	—	2980 (790%)	60	460	940	2230 (830%)	1030	2180	3490 (787%)	—	—	—
120	750	1560	2510 (880%)	—	—	780 (504%)	80	500	1070	2440 (830%)	1220	2240	3310 (777%)	—	—	—
150	1420	2770	3080 (820%)	—	—	420 (327%)	100	550	1160	2710 (830%)	1100	2240	3350 (777%)	20	40	80 (754%)
180	—	—	1900 (677%)	—	—	340 (280%)	120	600	1230	2670 (810%)	1150	2350	3200 (764%)	40	50	140 (937%)
	Time of cure [a] 135 min.			75 min.												
WITH LATEX-SPRAYED (WHOLE) RUBBER																
15	220	325	540 (900%) [b]	370	740	1280 (895%)	20	750	1500	2230 (773%)	840	1640	2360 (774%)	120	190	530 (940%) [b]
30	530	1050	2500 (955%)	880	1750	2710 (885%)	40	1070	2040	2630 (750%)	1300	2360	3010 (747%)	230	390	930 (860%) [b]
45	910	1790	2910 (890%)	1470	2750	3010 (825%)	60	1150	2300	2700 (733%)	1430	2680	2950 (724%)	300	550	1100 (834%) [b]
60	1630	2900	3180 (825%)	2220	—	2620 (740%)	80	1180	2290	2840 (747%)	1580	2949	3440 (745%)	360	750	1400 (820%) [b]
90	—	—	1560 (570%)	—	—	550 (380%)	100	1290	2420	2650 (720%)	1580	2910	3130 (727%)	440	910	1750 (837%) [b]
120	—	—	640 (387%)	—	—	540 (337%)	120	1320	2410	2700 (730%)	1600	2940	3340 (734%)	450	910	1930 (850%) [b]
	Time of cure [a] 49 min.			36 min.												

[a] Time in minutes to reach a modulus of 2100 lbs. per sq. in. at 800%. Such data are interpolated from the family of stress-strain curves for a given rubber. It has been found that the stress-strain curve passing through this point of reference also passes through the maximum (or very nearly so) in the time-tensile curve obtained from the series of cures. De Vries[13] employed such a point of reference in determining rate of cure. His value of 1.3 kg. per sq. mm. at 890% differs from that above, partly at least, because he used ring-shaped test-pieces of greater cross-sectional area.

[b] Jaw break.

Table III

Ingredients of Phosphate-Buffered Recipes, Press-Cured at 298° F

Recipe No.	D	DA	DB	DC	DD	DE	DF	DG	DH	DI	DJ	DK	DL	DM
Crepe rubber	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Sulfur	10	10	10	10	10	10	10	10	10	10	10	10	10	10
KH_2PO_4	—	0.86	0.82	0.74	0.64	0.54	0.45	0.36	0.27	0.18	0.09	0.9	—	—
$Na_2HPO_4.12H_2O$	—	0.12	0.24	0.48	0.72	0.96	1.20	1.44	1.68	1.92	2.16	—	2.39	1.28 [a]
pH of salts in 1/15 *M* aqueous soln.	—	5.6	5.9	6.2	6.4	6.6	6.8	7.0	7.2	7.4	7.7	4.5	9.0	4.0

[a] Potassium acid phthalate in this case.

In 1922 Bruce[2] published a set of the few analyses extant of the ash of various rubbers, including commercial sheet, commercial crepe, and a whole rubber prepared by evaporation of latex. The principal constituents of each ash were potassium and phosphorus. The ratios K_2O to P_2O_5 in the sheet and crepe were similar (approximately 0.55), whereas the ratio in the whole rubber was nearly 1.8. Bruce did not suggest, nor is it suggested here, that these elements were present in the rubber entirely as inorganic phosphates. Nevertheless, these data, together with those above on sodium acetate, might suggest that the latex-sprayed rubber cures faster than crepe because the serum material—that is, the nonrubber components—remaining in the finished crude is more alkaline in the case of L. S. rubber than in crepe. It has been known for many years that, in general, alkaline substances in a rubber-sulfur mix accelerate, whereas acidic substances retard curing. In a given series of rubbers showing naturally different rates of cure, it might be assumed that the acid-base equilibrium in the nonrubber components of those rubbers would form a gradation from an acidic to a basic condition. There is the further consideration that the serum substances remaining in a rubber like L. S. might have a greater buffer capacity in the presence of free hydrogen sulfide generated during curing than do serum substances in a rubberlike crepe. Biological fluids generally, including latex serum, are well buffered to resist changes in pH, and it may be to this portion of the serum solids—namely, the inorganic substances or the salts of organic acids or proteins remaining in the finished crude rubber—that the higher rate of curing is due.

EXPERIMENTAL

To ascertain whether this view has any possible basis, a well-washed first latex crepe and a whole rubber (L. S.) were chosen, similar to the ones described in Table I. These rubbers were compounded in both the rubber-sulfur and mercaptobenzothiazole test recipes but, except for two examples, discussion here will be confined to the former stock, as it illustrates the general trend. Into these batches was mixed a series of phosphate buffers of graded pH. Phosphate buffers were chosen because they were the most stable of a number tried in the presence of zinc oxide. Baker's reagent phosphates were used without further purification, and were added to give a 1/15 *M* concentration by weight on the rubber, as shown in Table III. The salts were dissolved in approximately an equal weight of distilled water, and were added to the rubber running with a rolling bank on the mixing mill by distributing the solution from a pipet over the back roll. Most of the water appeared to be lost during mixing, and no porosity of the cured sheets was observed. Any caking of the salts on the back roll was worked into the rubber by further addition of small quantities of water. Batches were run with potassium hydrogen phthalate, potassium dihydrogen phosphate, and disodium hydrogen phosphate alone, as well as with the buffer mixtures.

Recipe ingredients are shown on a batch weight basis, together with the pH value (to nearest tenth) of the salts in 1/15 *M* aqueous solution at room temperature. Curing and testing procedures were the same as those described above.

The general effect, in the case of first latex crepe, of more rapid cure with increase in alkalinity or reduction in rate of cure with increase in acid component, as shown in Table IV, is best visualized if the rate of curing, in minutes at 298° F, is plotted against pH of the salts in 1/15 *M* aqueous solution. Such a

TABLE IV

EFFECT OF INCREASE IN ACID COMPONENT ON RATE OF CURE OF PHOSPHATE-BUFFERED RUBBERS

Cure at 298° F (min.)	D (control)		DA		DB		DC		DD		DE		DF	
	700%	800%	700%	800%	700%	800%	700%	800%	700%	800%	700%	800%	700%	800%
TENSILE STRENGTH OF CREPE RUBBER IN POUNDS PER SQUARE INCH														
60	90	170	60	90	100	160	100	180	170	250	200	350	280	490
90	230	370	220	400	280	500	270	530	330	660	375	820	700	1490
120	370	750	400	800	550	1160	630	1360	770	1550	950	—	1400	2590
150	750	1620	920	1830	1070	2150	1180	2500	1510	—	1630	—	—	—
180	1220	2500	1640	—	1650	—	1870	—	2100	—	—	—	—	—
TENSILE STRENGTH OF CREPE RUBBER IN POUNDS PER SQUARE INCH (ELONGATION IN PER CENT)														
60	530 (1015%)		220 (1005%)		460 (985%)		550 (953%)		730 (950%)		800 (912%)		1510 (960%)	
90	1390 (990%)		1190 (970%)		1290 (940%)		1400 (930%)		1700 (933%)		1760 (885%)		2480 (890%)	
120	1910 (940%)		1680 (895%)		1900 (875%)		2230 (880%)		2320 (870%)		1620 (770%)[a]		2690 (815%)	
150	2600 (880%)		2360 (833%)		2630 (840%)		2730 (815%)		2420 (775%)		2440 (765%)		1660 (645%)	
180	2850 (825%)		2360 (760%)		2530 (765%)		2350 (735%)		2060 (697%)		975 (540%)		470 (377%)	
Time (min.[b])	169		157		149		142		136		129		107	
TENSILE STRENGTH OF LATEX-SPRAYED RUBBER IN POUNDS PER SQUARE INCH														
	700%	800%	700%	800%	700%	800%	700%	800%	700%	800%	700%	800%	700%	800%
15	260	500	280	470	260	490	240	400	260	470	240	400	270	450
30	560	1225	450	910	425	1110	450	900	420	900	450	920	550	1150
45	1030	2200	850	1800	1030	2150	960	1880	960	1840	860	1710	1225	2300
60	1725	1725	1650	—	1800	—	1670	—	1690	—	1660	—	1990	—
90	—	—	—	—	—	—	—	—	—	—	—	—	—	—
TENSILE STRENGTH OF LATEX-SPRAYED RUBBER IN POUNDS PER SQUARE INCH (ELONGATION IN PER CENT)														
15	920 (900%)		810 (880%)		940 (920%)		960 (940%)		1000 (910%)		930 (935%)		1280 (960%)	
30	2580 (923%)		2270 (935%)		2250 (917%)		2220 (935%)		2400 (955%)		1925 (910%)		2430 (920%)	
45	3100 (855%)		3010 (890%)		3040 (865%)		2500 (850%)		2900 (875%)		2720 (870%)		2975 (850%)	
60	2500 (763%)		2610 (775%)		2550 (765%)		2670 (790%)		2680 (785%)		2670 (790%)		2150 (715%)	
90	690 (430%)		625 (440%)		500 (370%)		670 (430%)		730 (450%)		700 (480%)		660 (410%)	
Time (min.[b])	44		47		45		48		49		49		42	

[a] Jaw break. [b] Minutes of cure to reach a modulus of 2100 lbs. per sq. in. at 800%.

TABLE IV—*Continued*

Cure at 298° F (min.)	DG		DH		DI		DJ		DK		DL		DM	
	700%	800%	700%	800%	700%	800%	700%	800%	700%	800%	700%	800%	700%	800%
TENSILE STRENGTH OF CREPE RUBBER IN POUNDS PER SQUARE INCH														
60	325	630	300	610	350	820	550	1150	110	200	590	1240	140	225
90	800	1650	1080	2190	1150	—	1300	—	260	420	1350	2480	250	450
120	1700	—	—	—	—	—	—	—	410	830	—	—	370	725
150	—	—	—	—	—	—	—	—	775	1630	—	—	670	1450
180	—	—	—	—	—	—	—	—	1270	2550	—	—	1100	2240
TENSILE STRENGTH OF CREPE RUBBER IN POUNDS PER SQUARE INCH (ELONGATION IN PER CENT)														
60	1425 (930%)		1610 (933%)		1920 (910%)		2120 (897%)		450 (980%)		2140 (880%)		440 (963%)[a]	
90	2590 (880%)		2600 (835%)		2040 (780%)[a]		2410 (795%)		1190 (965%)		2900 (830%)		880 (910%)	
120	2830 (785%)		1950 (730%)		1660 (660%)		590 (450%)		1810 (910%)		1060 (555%)		1500 (907%)	
150	1950 (655%)		460 (415%)		480 (380%)		540 (375%)		2280 (850%)		450 (365%)		2200 (860%)	
180	620 (417%)		350 (335%)		400 (330%)		470 (340%)		2550 (800%)		490 (350%)		2300 (805%)	
Time (min.[b])	101		89		88		82		165		81		174	
TENSILE STRENGTH OF LATEX-SPRAYED RUBBER IN POUNDS PER SQUARE INCH														
	700%	800%	700%	800%	700%	800%	700%	800%	700%	800%	700%	800%	700%	800%
15	350	660	300	560	280	590	330	570	240	410	300	575	170	290
30	610	1200	520	1210	525	1200	650	1300	420	900	580	1310	325	630
45	1200	2350	1100	2230	1130	2200	1290	2400	890	1920	1160	2250	570	1200
60	2030	—	2000	—	1960	—	2090	—	1670	2780	—	—	1300	2370
90	—	—	—	—	—	—	—	—	—	—	—	—	—	—
TENSILE STRENGTH OF LATEX-SPRAYED RUBBER IN POUNDS PER SQUARE INCH (ELONGATION IN PER CENT)														
15	1070 (885%)		1210 (920%)		1230 (936%)		1450 (942%)		690 (880%)		1225 (925%)		460 (895%)	
30	2250 (905%)		2530 (920%)		2325 (905%)		2520 (910%)		2330 (943%)		2550 (905%)		1800 (950%)	
45	2925 (835%)		2800 (840%)		2975 (855%)		3010 (945%)		3030 (876%)		2775 (840%)		2250 (890%)	
60	2540 (745%)		2250 (725%)		2210 (735%)		2250 (720%)		2780 (800%)		1730 (680%)		2490 (815%)	
90	960 (465%)		590 (395%)		530 (400%)		450 (365%)		860 (460%)		510 (375%)		750 (480%)	
Time (min.[b])	42		44		44		41		48		42		54	

[a] Jaw break. [b] Minutes of cure to reach a modulus of 2100 lbs. per sq. in. at 800%.

construction (Figure 1 is to be regarded as indicative of a possibility, not as a measured relation. Figure 1 suggests that, whereas the well-washed crepe is susceptible to treatment with buffer salts, L. S. rubber containing all the serum does not respond to any extent to the same concentrations of buffer salts; it behaves as though the serum material is of itself already an effective buffer.

If this were true, one might expect a wide variation in the rate of cure of rubber made from identical latex, depending on whether coagulation occurred on the acid or alkaline side and on the degree of effective washing the coagulum subsequently received. This has long been known to be the case.

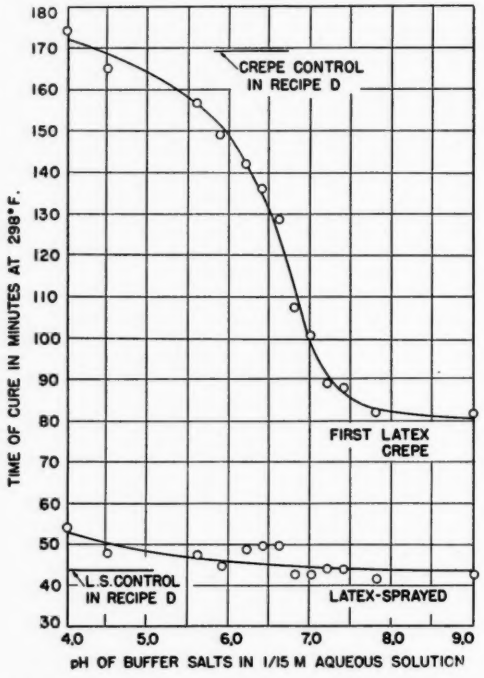

FIG. 1.—Effect of buffer salts on rate of cure of recipes D to DM, inclusive.

The presence of water in crepe rubber stock at the time of cure has an influence on the rate. This effect is shown in Figure 2, drawn on the same basis and with the same reservations as Figure 1. A sufficient quantity of distilled water was worked into each batch just before sheeting it off the mill. Under the conditions of open-mill mixing and overnight storage of the uncured but covered sheeted stock, accurate control of the average water content of each batch was not obtained, but it was measured. The extremes were 1.00 and 2.04 grams of water per 100 grams of rubber, the majority of the batches being near 1.5. These weights were taken just before the sheeted stock was placed in the curing moulds. Curing in this series was at 316° F, the object of this higher temperature being merely to speed up the test. The effect of the water was to spread the curve, the slow rubber curing more slowly, the fast rubber more rapidly, with minimum alteration in the rate of cure when the added buffers showed approximately

pH 6.6 in aqueous solution. It is possible that this effect was due to better or more effective distribution of the added phosphates throughout the rubber mass, but it will be noted that the control stock without any added phosphates was also affected by the presence of water.

Application of the treatment as a corrective measure in two supposedly acidic stocks is shown in Table V and VI. Table V compares air-dried acetic-acid-coagulated sheet, with and without added phosphate buffer salts (which alone in 1/15 *M* aqueous solution would show about pH 7.0), with air-dried alum-coagulated sheet, with and without added phosphate buffer salts. The stocks are based on the mercaptobenzothiazole recipe.

In the case of the alum-coagulated sheet, the presumed acidity was thought to arise from residual coagulant in the rubber, probably in association with protein. Whatever the cause, alum-coagulated rubber has long been known to cure extremely slowly. The data for compound AM-174 show this, all cures being very tender. Addition of phosphate buffer (2AX-174), however, produces a stock curing faster to a given modulus than the acetic control but, as might be expected, not so fast as the acetic control sheet containing the same quantity of added phosphates. Both the alum and acetic sheets were made by coagulation of aliquots of identical latex.

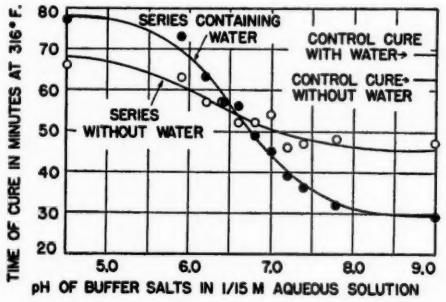

FIG. 2.—Effect of water in crepe rubber on rate of cure.

Corrective measures were also tried for slowing the cure experienced on addition of large volumes of channel gas black to vulcanizable stock (Table VI). These formulas are based on the mercaptobenzothiazole recipe. The trials arose from our observation that an aqueous slurry of channel gas black is acidic[17]. The data indicate that, with these particular stocks, the addition of the phosphate mixture (3AD-143) has approximately the same effect on the development of modulus as an additional 0.5 gram of mercaptobenzothiazole per 100 grams of rubber (3AE-143).

DISCUSSION

The hypothesis is suggested that a factor, perhaps a major one, in determining the rate of cure of rubber is the acid-base equilibrium developed during curing; it may be said for brevity (some may think inaccurately) that the pH of the system and its buffer capacity enable it to maintain a given reaction and thus condition the rate of cure of a given rubber. This assumed equilibrium could result in rubber-sulfur stocks, for example, from (1) the nonrubber components naturally present in the crude rubber mass, and (2) acidic substances, such as hydrogen sulfide[5], generated during vulcanization. The extent to which

TABLE V

TENSILE STRENGTHS OF ACETIC ACID- AND ALUM-COAGULATED STOCKS

Press Cure at 60° F (min.)	Acetic acid-coagulated sheet						Alum-coagulated sheet					
	AM-173 [a]			2AX-173 [b]			AM-174 [a]			2AX-174 [b]		
	600%	700%	At break	600%	700%	At break	600%	700%	At break	600%	700%	At break
30	570	1160	2230 (820%)	1100	2230	3310 (775%)	90	150	300 (830%)	740	1460	2430 (790%)
45	775	1500	2700 (800%)	1290	2540	3290 (760%)	175	300	600 (810%)	850	1740	2650 (780%)
60	840	1780	2900 (800%)	1310	2580	3400 (770%)	230	420	1090 (840%)	980	1970	2900 (775%)
75	890	1780	3000 (780%)	1520	2620	2940 (730%)	280	510	975 (800%)	1020	1990	2990 (775%)
90	960	1950	3100 (810%)	1310	2575	3200 (750%)	310	610	1420 (850%)	1030	2040	2940 (775%)
120	940	1890	3160 (800%)	1375	2620	3290 (750%)	350	690	1600 (860%)	1010	1940	2940 (780%)

[a] Rubber 100, zinc oxide 6, sulfur 3.5, mercaptobenzothiazole 0.5, stearic acid 0.5.
[b] Rubber 100, zinc oxide, 6, sulfur 3.5, mercaptobenzothiazole 0.5, stearic acid 0.5, $NaH_2PO_4.H_2O$ 0.37, K_2HPO_4 0.70.

TABLE VI

TENSILE STRENGTHS OF CHANNEL BLACK STOCKS

Press Cure at 260° F (min.)	0.5 mercaptobenzothiazole/100 rubber						1.0 mercaptobenzothiazole/100 rubber					
	3AC-143 [a]			3AD-143 [b]			3AE-143 [c]			3AF-143 [d]		
	400%	500%	At break	400%	500%	At break	400%	500%	At break	400%	500%	At break
30	890	1275	2300 (710%)	1320	1900	2700 (625%)	1030	1590	2580 (670%)	1710	2440	3920 (660%)
45	1220	1900	2660 (640%)	1625	2300	3375 (630%)	1490	2220	3275 (640%)	1930	2770	4000 (650%)
60	1610	2260	3010 (600%)	1840	2630	3575 (625%)	1760	2530	3700 (650%)	2200	3090	4340 (640%)
90	1990	2760	3475 (590%)	2090	2920	3450 (560%)	2050	2875	3900 (610%)	2420	3375	4100 (575%)

[a] Rubber (first latex crepe) 100, zinc oxide 6, sulfur 3.5, mercaptobenzothiazole 3.5, stearic acid 2.5 channel black 50.
[b] Same as 3AC-143 plus 0.37 $NaH_2PO_4.H_2O$ and 0.70 K_2HPO_4.
[c] Rubber (first latex crepe) 100, zinc oxide 6, sulfur 3.5, mercaptobenzothiazole 1.0, stearic acid 2.5, channel black 50.
[d] Same as 3AE-143 plus 0.37 $NaH_2PO_4.H_2$ and 0.70 K_2HPO_4.

hydrogen sulfide would influence the equilibrium would depend on its rate of formation and rate of removal—that is, its concentration at any given time. Even with the same rubber, this concentration (and resulting acid-base equilibrium) would be expected to be different in the case of rubber-sulfur stocks (assuming high concentrations of hydrogen sulfide) compared with accelerated stocks (assuming low concentration of hydrogen sulfide). Moreover, it might be expected to vary with the type of accelerator used. Addition of various reinforcing agents or fillers, particularly in large volume, could be expected to affect the acid-base equilibrium; but any such effect, on the whole due to addition of standard pigments, would probably be of less magnitude if the batch were compounded with a whole rubber, such as L. S. made from ammoniated latex, than if it were compounded with well-washed (but unfermented) rubbers such as first latex crepe.

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POLYSULFIDE THEORY OF ACCELERATOR ACTION DURING VULCANIZATION

EVIDENCE FOR THE THEORY *

Ross E. Morris

Rubber Laboratory, Navy Yard, Mare Island, Calif.

On the basis of indirect experimental evidence, Scott and Bedford[5] proposed about twenty years ago a mechanism of the accelerator action of metallic dithiocarbamates, known as the polysulfide theory. According to these authors, a metallic dithiocarbamate reacts with sulfur during vulcanization to form a polysulfide, which subsequently decomposes and liberates active sulfur for reaction with the rubber hydrocarbon. This theory gained support by the observation of Jones and Depew[2] that the solubility of zinc dimethyldithiocarbamate in rubber is increased when sulfur is added to the mix, since such behavior may result from the formation of a soluble polysulfide. More recently, Scott and Sebrell[6] questioned Scott and Bedford's polysulfide theory, on the basis that no polysulfides of metallic dithiocarbamates have been isolated.

The author does not intend to enter into the controversial subject of the mode of action of vulcanization accelerators, but rather to present experimental data which confirms the original supposition of Scott and Bedford that sulfur forms unstable addition compounds, or polysulfides, with metallic dithiocarbamates. The metallic dithiocarbamates investigated were zinc diethyldithiocarbamate and zinc dibutyldithiocarbamate.

PRELIMINARY WORK

Inasmuch as zinc dithiocarbamate accelerators bring about vulcanization of rubber or rubber cements at room temperature, polysulfides of zinc dithiocarbamates should be formed at this temperature if the polysulfide theory is correct. The author dissolved sulfur and zinc diethyldithiocarbamate, in approximately equimolecular proportions, in benzene at 30° C, and evaporated the solvent at temperatures ranging from 35° to 50° C. The residue apparently consisted of white zinc diethyldithiocarbamate crystals and yellow sulfur crystals, with no evidence of a polysulfide. The identity of the crystals was confirmed by carrying out a mixed melting point determination with pure zinc diethyldithiocarbamate in the case of the white crystals, and analyzing for zinc in the case of the yellow crystals. The white crystals did not lower the melting point of zinc diethyldithiocarbamate, and the yellow crystals did not contain zinc. A similar experiment was performed with sulfur and zinc dibutyldithiocarbamate, with the same results. It is evident that zinc dithiocarbamates do not react with sulfur to form stable polysulfides.

The results of these experiments do not necessarily preclude the possibility that unstable polysulfides of zinc dithiocarbamates exist. Langenbeck and Rhiem[3]

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were unable to isolate a polysulfide from a solution of sulfur and benzothiazyl disulfide in carbon disulfide, but they proved the existence of several unstable polysulfides of benzothiazyl disulfide by means of a fusion diagram. An attempt was made by the author to apply this method to the present problem. Various proportions of sulfur and zinc dibutyldithiocarbamate were fused together, the fusion mixtures were allowed to solidify, and the behavior of the mixtures in a melting point apparatus was studied. Unfortunately it was found that melted sulfur and melted zinc dibutyldithiocarbamate are not miscible in all proportions. Such behavior complicates the analysis of a fusion diagram, so further work in this direction was abandoned.

The author then turned to the classical method for determining the decomposition constants of complex addition compounds discovered by Behrend[1]. This method depends on the measurement of solubility alterations in suitable heterogeneous systems. For example, the apparent solubility of compound *A* in a solvent is increased when a reactive compound *B* is dissolved in the saturated solution, because some of compound *A* reacts with compound *B* to form the soluble addition compound *AB*. Although the logical system to study in this case would be rubber-sulfur-zinc dithiocarbamate, such a system would reach equilibrium only very slowly because of the high viscosity of rubber; and accurate solubility measurements would be impossible because rubber undergoes a chemical reaction with sulfur in the presence of the ultra-accelerator. It was decided to employ benzene and cyclohexane as solvents for the following reasons. They are hydrocarbons as is rubber, they are liquids which may be readily purified, the molecular condition of dissolved substances may be accurately determined by the cryoscopic method, and information concerning the existence of addition compounds in these solvents may be later employed for studying the vulcanization of cements.

MEASUREMENT OF SOLUBILITY ALTERATIONS

Preparation of Materials

Baker's C. P. benzene was fractionated, and the fraction having a freezing point of 5.5 C or above, was used.

Eastman's P702 cyclohexane was repeatedly fractionated, and the fraction having a freezing point of 6.0 C, or above was used.

Commercial 99.5 per cent sulfur was crystallized once from toluene. The crystals were washed with acetone and dried in air with slight warming.

Commercial Ethyl Zimate was used as the source of zinc diethyldithiocarbamate. This was recrystallized four times from toluene containing a little ethanol. Solution was effected for the first two crystallizations by boiling in the presence of bone charcoal. The material used in the solubility measurements was in the form of white crystals, having a melting point of 177.7° C.

Commercial Butyl Zimate was used as the source of zinc dibutyldithiocarbamate. This was recrystallized three times, using the solvents and procedure described for zinc diethyldithiocarbamate. The material used in the solubility measurements was in the form of white crystals, having a melting point of 107.3° C.

Procedure

The solubility equilibrium was attained in a glass-stoppered, 250-cc. flask immersed in a water-bath maintained at 30° ± 0.03° C. Approximately 55 cc. of

solvent were used. The solution was agitated by an electromagnetic stirrer in the flask. At least 48 hours was allowed for reaching saturation. The saturated solution was transferred by means of air pressure to a 50-cc. wide-mouth flask with cork stopper, which had been previously weighed with and without the cork stopper. The liquid was filtered through two layers of fine linen during transfer. The flask, closed with the cork stopper, was again weighed. The cork stopper was removed, and the flask dried to constant weight over a 10-watt electric lamp. The temperature of the liquid during evaporation ranged from 35° to 50° C, depending on room temperature. It had been previously found that no oxidation of zinc dithiocarbamates or sublimation of sulfur takes place after several weeks of heating in this temperature range.

The solubilities of the pure substances in benzene and in cyclohexane were determined before proceeding with the investigation of three-component systems. The solubility data are given in Table I. The solubility of each of the three sub-

TABLE I

SOLUBILITY OF PURE SUBSTANCES AT 30° C

	Grams	100 grams solvent
Sulfur	2.517	Benzene
Zinc diethyldithiocarbamate	3.872	Benzene
Zinc dibutyldithiocarbamate	12.80	Benzene
Sulfur	1.409	Cyclohexane
Zinc diethyldithiocarbamate	0.103	Cyclohexane
Zinc dibutyldithiocarbamate	8.992	Cyclohexane

stances in benzene is greater than it is in cyclohexane. This difference is particularly large in the case of zinc diethyldithiocarbamate.

In order that the thermodynamic activities of the solutes should not differ to any extent from their respective concentrations and thus complicate the analysis of the data, it was necessary that a system be selected in which the solubility of the solid phase would not be excessive. At the same time, for convenience and accuracy, it was desirable that the solubility of the solid phase should not be too low. Accordingly, the systems in Table II were selected for investigation. No solubility determinations were made with zinc dibutyldithiocarbamate as the solute at saturation, because its solubility was considered too high. The results of the solubility determinations are shown graphically in Figures 1 to 4.

ANALYSIS OF DATA

In each of the systems investigated, the solubility of the solid phase increases in direct proportion to the concentration of the third component. The fact that the relation is of the first order in the system sulfur-zinc diethyldithiocarbamate-benzene, when either of the solutes is at saturation, is particularly significant, since it proves that one molecule of sulfur combines with one molecule of zinc diethyldithiocarbamate to form one molecule of the addition compound.

The veracity of the last statement is readily demonstrated. Consider the bimolecular reaction:

$$A+B \rightleftharpoons AB$$

to reach equilibrium in a solvent. The equilibrium constant can be written:

$$K=\frac{(AB)}{(A)(B)}$$

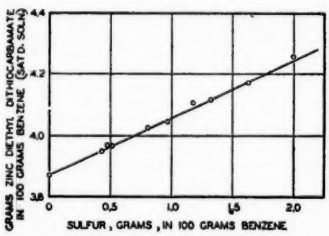

FIG. 1.—Solubility of zinc diethyldithiocarbamate in solutions of sulfur in benzene.

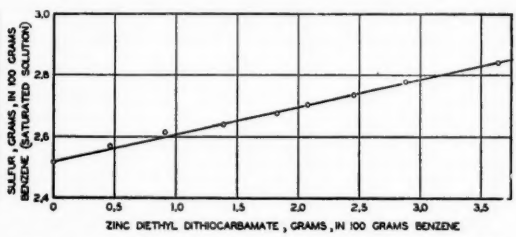

FIG. 2.—Solubility of sulfur in solutions of zinc diethyldithiocarbamate in benzene.

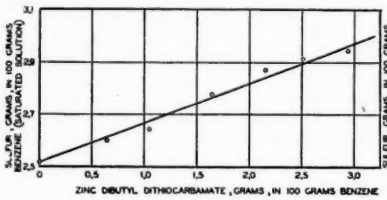

FIG. 3.—Solubility of sulfur in solutions of zinc dibutyldithiocarbamate in benzene.

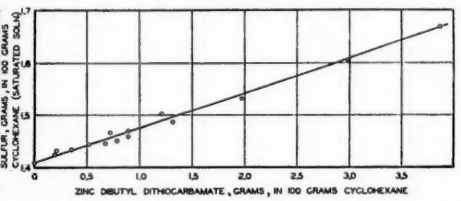

FIG. 4.—Solubility of sulfur in solutions of zinc dibutyldithiocarbamate in cyclohexane.

TABLE II

SYSTEMS SELECTED FOR INVESTIGATION

Solvent	Solute at variable concn.	Solute at Satn.
Benzene	Sulfur	Zinc diethyldithiocarbamate
Benzene	Zinc diethyldithiocarbamate	Sulfur
Benzene	Zinc dibutyldithiocarbamate	Sulfur
Cyclohexane	Zinc dibutyldithiocarbamate	Sulfur

Let sufficient solid compound A be added so that the solution will remain saturated with respect to A. Then the concentration of A in the solution will remain constant in spite of reaction of A with B, and the equilibrium constant can be written:

$$K_1 = \frac{(AB)}{(B)}$$

$$\text{or} \quad (B)K_1 = (AB)$$

Since, in the experimental method used, the amount of AB in solution is not directly determined as such, but is calculated from the apparent increase in solubility of A, the latter value is directly proportional to the concentration of B. In other words, when the increase in solubility of A per 100 grams of solvent is plotted against the concentration of B per 100 grams of solvent, a straight line will result. The same reasoning is applicable to the case where the solution is saturated with respect to B and the concentration of A is variable.

On the other hand, if the reaction takes place as follows:

$$2A + B \rightleftharpoons A_2B$$

$$\text{or} \quad A + 2B \rightleftharpoons AB_2$$

or in any other manner where more than one molecule of A or B is involved, the reasoning above will show that at least one of the curves, obtained by plotting

the apparent increase in solubility of the substance at saturation against the variable concentration of the other substance, is not a straight line.

The linear relations between the concentration of zinc dibutyldithiocarbamate and the proportion of sulfur required to saturate the solution in benzene or cyclohexane (Figures 3 and 4) prove that one molecule of zinc dibutyldithiocarbamate reacts with sulfur to produce one molecule of the addition compound. No information can be gained from these curves as to the number of molecules of sulfur which enter into the reaction. It seems reasonable, however, that this reaction should proceed in the same manner as the reaction between zinc diethyldithiocarbamate and sulfur.

CALCULATION OF EQUILIBRIUM CONSTANTS

The composition of the addition compounds may be ascertained by determining the molecular weights of sulfur and the zinc dithiocarbamates in the solvents used. These values were determined in benzene by the cryoscopic method. The results (Table III) prove that sulfur in solution is in the form of S_8 molecules, and that zinc dithiocarbamates exist as unassociated molecules. It is concluded, therefore, that the reaction takes place as follows:

$$S_8 + Zn(SCSNR_2)_2 \rightleftarrows Zn(SCSNR_2)_2 . S_8$$

where R is a hydrocarbon radical. The equilibrium constant for this reaction may be written:

$$K = \frac{[Zn(SCSNR_2)_2 . S_8]}{[S_8][Zn(SCSNR_2)_2]}$$

where each term in the fraction represents the concentration of that ingredient in moles per 1000 grams of solvent.

TABLE III

MOLECULAR WEIGHTS IN BENZENE BY CRYOSCOPIC METHOD

Substance	Molecular weight	
	Found	Theoretical
Sulfur(S_8)	255	256
Zinc diethyldithiocarbamate	366	362
Zinc dibutyldithiocarbamate	469	474

Using the slope of the line in the graph and the solubility of the solid phase from Table I, it is possible to calculate the equilibrium constant, K, for each of the systems investigated. The values of K for the various reactions are given in Table IV. The reaction between sulfur and zinc dibutyldithiocarbamate is assumed to be bimolecular for the purpose of this calculation although, as pointed out above, the order of this reaction is not definitely known.

The values calculated for the equilibrium constant of the sulfur-zinc diethyldithiocarbamate reaction in benzene from different solubility data are in good agreement (Table IV). Also, the values calculated for the equilibrium constant of the sulfur-zinc dibutyldithiocarbamate reaction in benzene and cyclohexane, respectively, are different, the magnitude of the values indicating that the sulfur-zinc dibutyldithiocarbamate addition compound is more stable in benzene than it is in cyclohexane.

TABLE IV

EQUILIBRIUM CONSTANTS AT 30° C

Reacting substances	Solute at saturation	Solvent	Equilibrium constant K
S_8 + Zn diethyldithiocarbamate	Zn diethyldithiocarbamate	Benzene	1.41
S_8 + Zn diethyldithiocarbamate	Sulfur	Benzene	1.45
S_8 + Zn dibutyldithiocarbamate	Sulfur	Benzene	3.91
S_8 + Zn dibutyldithiocarbamate	Sulfur	Cyclohexane	2.57

TABLE V

RUBBER CEMENTS

	A	*B*
Benzene	100.0	100.0
Pale crepe	5.0	5.0
Zinc oxide	0.5	0.5
Sulfur	1.0	1.0
Zinc diethyldithiocarbamate	1.5	—
Zinc dibutyldithiocarbamate	—	1.965

RELATIVE ACTIVITY OF ACCELERATORS

It should be emphasized that the equilibrium data reported here cannot be used as a measure of the relative activity of these compounds as vulcanization accelerators because there is, in general, no connection between equilibrium constant of a reaction and the rate of the reaction. Although the magnitude of the equilibrium constants given in Table IV indicates that sulfur forms a more stable addition compound with zinc dibutyldithiocarbamate than it does with zinc diethyldithiocarbamate, it does not follow that the former compound is the more active accelerator; in fact, as shown below, the contrary is true.

The relative activities of zinc diethyl- and zinc dibutyldithiocarbamates as vulcanization accelerators were found by observing the time required at 30° C for the cements given in Table V to gel. The accelerators in these cements were in equimolecular proportions, and within their respective solubility limits. Cement *A* gelled in 2 days, whereas cement *B* required 3 days to reach the same consistency. Evidently zinc diethyldithiocarbamate is the more active accelerator, nothwithstanding the relatively greater instability of its sulfur addition compound.

OTHER EVIDENCE FOR POLYSULFIDE THEORY

In conclusion, the author acknowledges that, in verifying the existence of an addition compound between sulfur and a zinc dithiocarbamate, he has not fully confirmed the accelerator mechanism proposed by Scott and Bedford[5] because he has presented no evidence to prove that the addition compound is actually involved in the vulcanization reaction. However, support of the argument that the addition compound is involved in the vulcanization reaction may be found in the discussion by Lewis, Squires, and Nutting[4]. These authors pointed out that the peculiar shape of the curves for combined sulfur *vs.* time of cure may be readily explained if it is assumed that the accelerator and sulfur react to form a sulfur complex which, in turn, reacts with the double bonds of the rubber to form rubber sulfide and thus regenerates the accelerator.

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SWELLING OF SYNTHETIC RUBBERS IN MINERAL OILS [1]

SWELLING IN MINERAL OILS CONTAINING POLYOLEFINS AND IN MIXTURES OF NUJOL AND BIPHENYL *

P. O. Powers and H. A. Robinson

Armstrong Cork Company, Lancaster, Penna.

An earlier paper[4] in this series showed that the aniline point of a mineral oil is a useful index of its tendency to swell synthetic rubber compositions. That article brought out that one oil (No. 9) of the series investigated gave a different slope for the cloud point curve at various concentrations of aniline from the other oils investigated. It was suggested that the unusual behavior of this oil might be due to the presence of added polyolefins. This view has been substantiated by a study of mixtures of mineral oil and polyolefins and of commercial lubricating oils known to contain such added materials. Polyolefins are added to mineral oils to improve their viscosity index[7].

EFFECT OF MINERAL OIL-POLYOLEFIN MIXTURES ON SYNTHETIC RUBBER

A proposed method for the determination of the aniline point of mineral oils[1] called attention to the possible interference of a turbidity caused by "petroleum products which are not strictly petroleum oil". This method is essentially that used by the authors, except that the A. S. T. M. determination was made on a 50 per cent mixture by volume rather than by weight, and that agitation was mechanical rather than manual.

Fraser[5] noted the "pseudoaniline point" which occurs when polyolefins are present in mineral oils. He recommends taking the temperature at which a permanent cloud appears on cooling, and also the temperature at which it disappears on warming. The two cloud points should not differ by more than 0.5° F.

Determination of Aniline Point

The method of the earlier paper[4] was used in determining the aniline point. This is the temperature at which the aniline and mineral oil separate, and must not be confused with a haze point which occurs at a higher temperature, due to separation of the polyolefin from the mineral oil-aniline mixture. In most cases this is only a slight haze and does not obscure the aniline point, which is marked by a sudden and pronounced turbidity. It has been found that a definite two-layer separation of the liquids takes place just below the true aniline point. Since this does not happen at the haze point, the two-phase separation is a valuable check on whether or not the true aniline point has been reached. This separation takes place from 1° to 2° C below the aniline point, and occurs as soon as agitation is stopped.

Figures 1 and 2 show cloud and haze points of the oils used. The haze tem-

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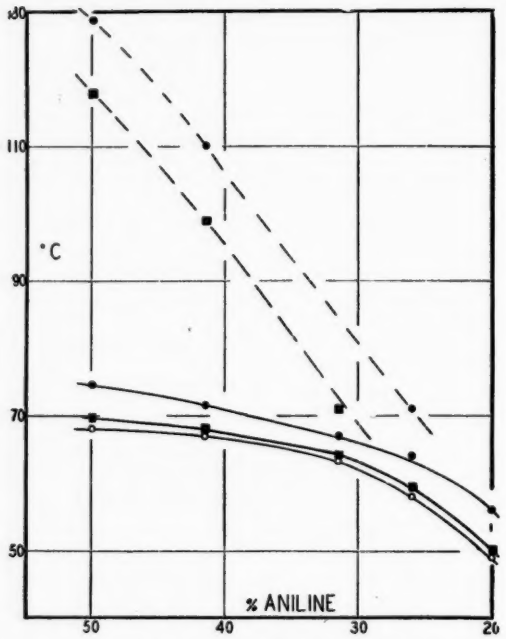

FIG. 1.—Cloud and haze point of oils containing added polyolefins in aniline at various concentrations.

——— Cloud points.
— — — Haze points.
○ Low aniline-point mineral oil.
■ Low aniline-point mineral oil with 2.5 per cent polybutene.
● Low aniline-point mineral oil with 10 per cent polybutene.

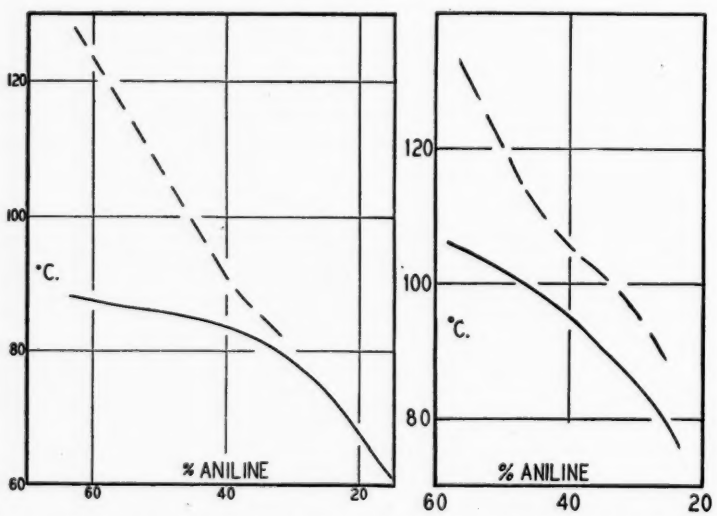

FIG. 2.—Cloud and haze points of hydraulic oil (*left*) and of Mineral Oil (*right*) in Aniline.

——— Cloud point.
— — — Haze point.

peratures approach the cloud temperatures at low concentrations of aniline. Where the haze is pronounced, the shape of the cloud point curve at a low concentration of aniline helps indicate the cloud temperatures at higher concentrations of aniline. At 60 per cent aniline and above, the haze may make the aniline point difficult of observation but, since the cloud point at 50 per cent aniline by weight has been found to be a satisfactory index of the swelling characteristics of mineral oils[4], the critical solution temperature of these oil-aniline mixtures was not determined.

Rubber Compositions

Three synthetic rubber stocks were used. They had been evaluated previously in swelling tests, and are believed to be representative of commercial stocks.

Composition A was a Neoprene, Type G, compound containing 70 volumes of soft carbon black (Thermax) per 100 volumes of Neoprene, Type G.

Composition C was a Perbunan Extra compound containing 53 volumes of carbon black and 9 volumes of extractable softener per 100 volumes of Perbunan.

Composition E was a Thiokol-DX composition containing a total of 125 volumes of carbon black and cork dust per 100 volumes of Thiokol.

All these compounds were prepared in sheet form by vulcanizing in a tensile sheet mould to the same extent as used in commercial practice.

Mineral Oils

Two oils were obtained on the open market. One was a hydraulic oil, the other, an SAE-30 motor oil; both were known to contain polybutenes. Mixtures of a low aniline-point mineral oil with Vistanex-7000 (a polybutene of approximately 7000 molecular weight) were made; 2.5 and 10 parts of Vistanex were used per 100 parts of mineral oil.

Procedure and Results

Duplicate samples of each stock, $1\times2\times0.1$ inch ($2.5\times5\times0.25$ cm.) were placed in the different oils, and the percent volume increases were determined after 1, 2, 3, 4, 6, and 12 weeks' immersion in small individual stoppered bottles held in a constant-temperature cabinet at $70°\pm1°$ C. Volume change was determined by the displacement method according to the procedure of the A. S. T. M.[3]

The swelling-time curves are shown in Figure 3. For Figure 4, three curves were taken from the previous article[4]. They show the aniline point-swelling relations for the three synthetic rubbers discussed in this paper. The points plotted are from data obtained with the mineral oils containing polyolefins. It is clear that the percentage swelling follows the true aniline point as in the previous work.

Fraser[5] studied the swelling of a Neoprene, Type G, composition in lubricating and hydraulic oils containing polyolefins. He found that swelling in these oils could be measured by the aniline point. The tests were made at 100° C, with five different types of oils.

The results with the synthetic mixture (Figure 4, above) show that addition of a polyolefin to a mineral oil results in slightly lower swelling. The results indicate that haze point is not a measure of swelling tendency, but that the aniline point is a useful index, and has the same significance that it does with other mineral oils.

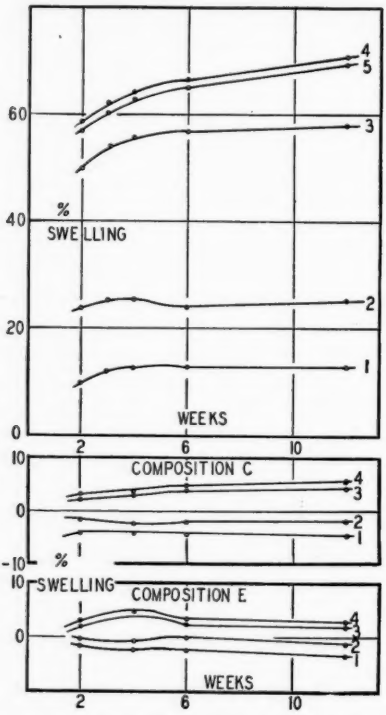

FIG. 3.—Swelling of black-loaded Neoprene (*above*) and of compositions C and E in oils containing polyolefins.

1. Motor oil.
2. Hydraulic oil.
3. Low aniline-point mineral oil with 10 per cent added polybutene.
4. Low aniline-point mineral oil.
5. Low aniline-point mineral oil with 2.5 per cent added polybutene.

SWELLING OF NEOPRENE IN NUJOL-BIPHENYL MIXTURES

A series of standard liquids for measuring the swelling of various synthetic rubbers in the laboratory would be very useful. Such liquids should be obtainable in pure form and be highly reproducible. Nujol-biphenyl mixtures seem to fulfill these requirements.

Nujol, a white refined mineral oil, is readily available. Examination of several samples showed a 3° C maximum variation of the aniline point. Its swelling effect on various samples of synthetic rubber compositions may, therefore, vary by the amount expected from this range. A highly refined material of higher aniline point than Nujol is not readily available. Paraffin wax probably comes closest to meeting this requirement, but commercial samples have been found to vary by as much as 10° C in their aniline points.

Many automotive lubricating oils have higher aniline points than Nujol. It is not definitely known how much variation can be expected in the aniline points of various samples of any one commercial oil of this type. If such a high aniline-point oil is available with no greater variation than is encountered with Nujol, mixtures of this oil with biphenyl would have a wider range of aniline points

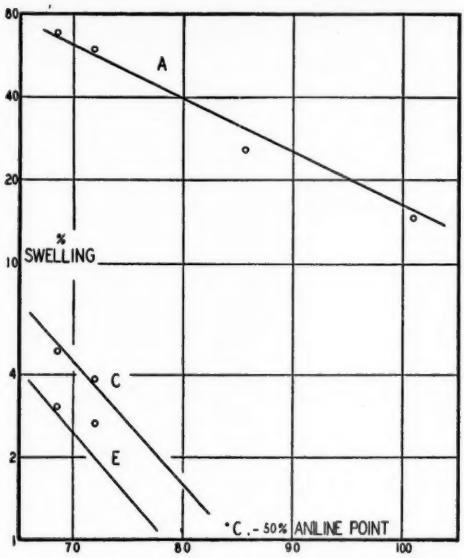

FIG. 4.—Aniline point of oil *vs.* percentage swelling.

than the mixtures employed in this study, but would probably have many of the same deficiencies.

Biphenyl is readily available in a high state of purity and, as a result of its aromatic structure, should show a high tendency to swell synthetic rubbers.

PREPARATION OF MIXTURES

Biphenyl was obtained from the Dow Chemical Company (melting point 70° C), and was used without further purification. Nujol was purchased in the open market. The mixtures of Nujol and biphenyl were made on a weight basis, and were homogeneous at the temperature of the test. Crystallization of the biphenyl occurs when over 20 per cent is present. Since mixtures rich in biphenyl are practically solid at room temperature, they are not so easily handled as mineral oils.

The aniline points of the Nujol-biphenyl mixtures were determined by the method described[4]. In all cases, the percentages are by weight. Figure 5 shows the 50 per cent (by weight) aniline point for various Nujol-biphenyl mixtures. Figure 6 shows the cloud temperatures in the ternary system Nujol-biphenyl-aniline.

PROCEDURE AND RESULTS

Composition A, containing 70 volumes of soft carbon black (Thermax) per 100 volume of Neoprene, Type G, was used. It was prepared in sheet form by vulcanizing in a standard tensile sheet mould to the same extent as used in commercial practice. Samples of the Neoprene compound were immersed in Nujol-biphenyl mixtures containing 20, 45, 60, 70, and 80 per cent of Nujol. The percentage volume increases were measured after 1, 2, 3, 4, 6, and 12 weeks' immersion in small individual stoppered bottles in a constant-temperature cabi-

net at 70° ± 1° C. The volume changes were determined by the A. S. T. M. method[3].

The time-swelling curves for the various mixtures are shown in Figure 7. Figure 8 correlates the swelling of the Neoprene in the biphenyl-Nujol mixtures

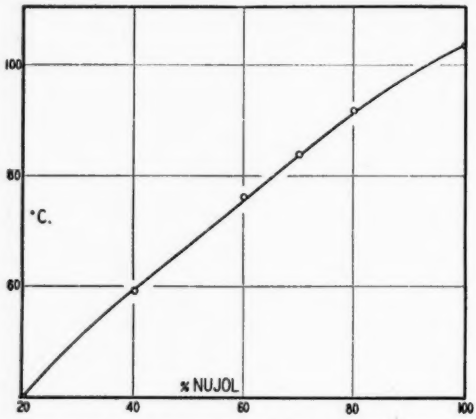

FIG. 5.—Aniline point (50 per cent by weight) of Nujol-biphenyl mixtures.

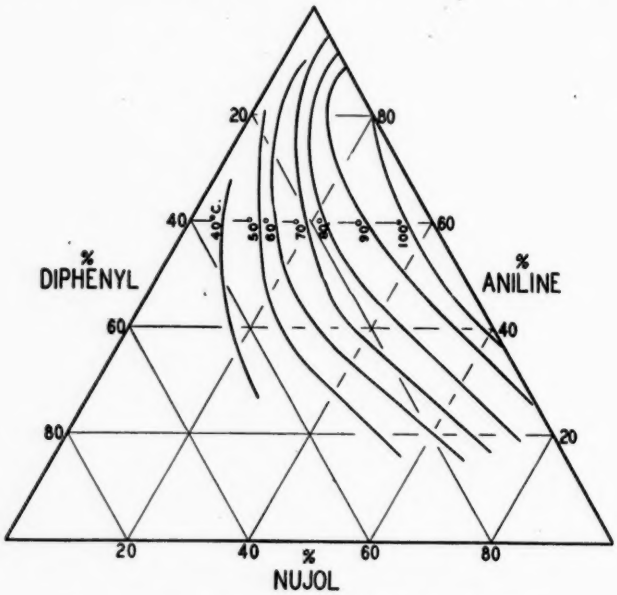

FIG. 6.—Cloud point of Nujol-biphenyl-aniline mixtures.

and in mineral oil with the same aniline point. The swelling at high concentrations of Nujol obviously approaches that of mineral oil, since the swelling in pure Nujol must fall on the mineral oil curve.

Since biphenyl is of lower molecular weight than the mineral oils, it may diffuse into the synthetic rubber composition more rapidly and thus give the

effect of a lower aniline point oil. Such selective absorption of a solvent was noted previously[6].

When high swelling was encountered, as when mixtures rich in biphenyl were

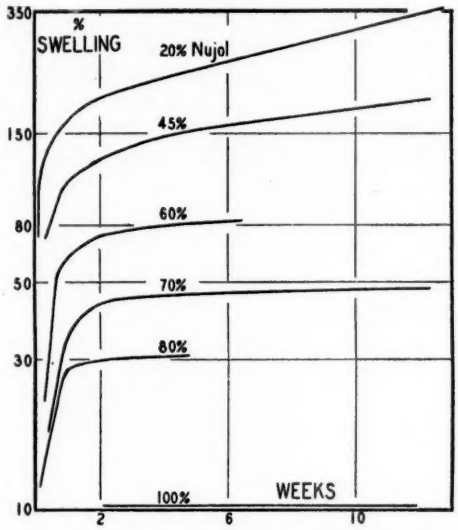

FIG. 7.—Swelling of Neoprene composition in Nujol-biphenyl mixtures.

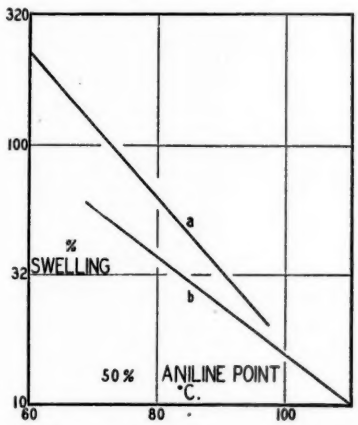

FIG. 8.—Aniline point *vs.* per cent swelling of Neoprene composition.

a. Nujol-biphenyl mixtures.
b. Mineral oils.

used, equilibrium was not reached in 12 weeks (Figure 7). This effect was also noted with mineral oils of low aniline point.

Perbunan and Thiokol compounds containing carbon black were tested in the mixture containing 30 per cent diphenyl. Both compounds gave appreciably greater swelling than would be expected from mineral oils of the same aniline

point. These compounds were not tested with other Nujol-biphenyl mixtures, but it is apparent that synthetic rubber compositions do not in general show the same correlation between aniline point and swelling as do mineral oils.

CONCLUSIONS

The true cloud temperature of a 50-50 weight mixture of aniline and mineral oil is a reliable index of the amount of swelling a synthetic rubber undergoes when immersed in mineral oil. This result is also true of mineral oils which contain polyolefins. Since the presence of both haze and cloud points is characteristic of such oils when mixed with aniline, a method has been worked out for distinguishing between them. Conversely, the presence of both haze and cloud points is believed to be indicative of the fact that polyolefins have been added to the mineral oils.

The addition of polyolefins to mineral oils reduces the tendency of those oils to swell synthetic rubbers. The logarithm of the percentage swelling varies inversely with the aniline point.

Although mixtures of Nujol and biphenyl can be duplicated fairly well, they offer no advantage over mineral oils for testing the tendency of synthetic rubber compositions to swell. Although the logarithm of swelling decreases as the 50 per cent aniline of the mixture increases, the relationship is not the same as that found for mineral oils.

For evaluating behavior under service conditions, immersion tests in oils having the same aniline point as oils which may be encountered in service are believed to be more reliable and more significant.

REFERENCES

[1] Strictly speaking, the term "synthetic rubbers" is incorrect, since these rubberlike substances are not the molecular duplicates of natural rubber. Other names have been proposed, such as "elastomers" (by H. L. Fisher); but in the absence of any accepted and uniform nomenclature, industry seems to have adopted the term "synthetic rubber", and that designation has become common parlance.
[2] Am. Soc. Testing Materials, *Proceedings*, **40**, Appendix II, 3B (1940).
[3] Am. Soc. Testing Materials, Standards, Pt. 3, p. 837, designation D471-37T (1939).
[4] Carman, Powers, and Robinson, *Ind. Eng. Chem.* **32**, 1069 (1940).
[5] Fraser, RUBBER CHEM. TECH., **14**, 204 (1941).
[6] Smith, U. S. Patent 2,209,940 (1940).
[7] Thomas, Zimmer, Turner, Rosen and Frolich, *Ind. Eng. Chem.* **32**, 301 (1940).

EFFECTS OF LOW TEMPERATURES ON NEOPRENE VULCANIZATES *

FELIX L. YERZLEY [1] and DONALD F. FRASER

E. I. DU PONT DE NEMOURS & COMPANY, INC., WILMINGTON, DELAWARE

The development of rubberlike materials to resist the effect of extreme cold is becoming increasingly important to the progress of engineering design, particularly in the automotive and aviation industries. While this development has progressed rapidly, more rapid progress will be possible when the properties to be improved are more clearly defined and when standard methods of evaluation have been adopted. Comparisons of results between laboratories have been made extremely difficult by the variety of tests and methods of interpretation. It is recognized that the physical factors are too complicated to permit a ready and practical solution of the problem by a single test procedure. The purpose of this paper is to describe and discuss the advantages and limitations of various test procedures used by the du Pont rubber laboratories. Certain features of the tests have been unique and are described in the hope that they may suggest further improvements in test methods. Yet, in spite of the limitations of the tests, they have suggested compounding improvements of familiar types of Neoprene and the development of an entirely new type of Neoprene, with superior resistance to the effects of low-temperature exposure.

The elasticity of materials may be used as a basis for measurements at low temperatures to determine the effects of continued exposure. The two aspects which are most obvious are changes in modulus and changes in resilience. The indications of change in modulus can be obtained by tests in tension, torsion, bending, or compression. Tests for changes in resilience can be made, with the proper temperature control, by one of the familiar types of resiliometer.

In addition to the foregoing methods, which represent a direct approach to the engineering problem by the measurement of mechanical properties, there are the indirect method of the T-50 test and methods which may be important in fundamental studies, including measurements of heat capacity[3] and dimensional changes[7] at various temperatures. The indirect methods generally imply a change in physical structure of materials as a result of transition from an amorphous form to a crystalline form on continued exposure to cold.

Two distinct demands must be met by rubberlike materials to perform satisfactorily at low temperatures. The first is that the material remain sufficiently flexible to resist fracture by impact or by probable mechanical strains. The second is the maintenance of functional characteristics—for example, in motor mountings so that the spring rate and damping characteristics is not changed enough to disturb dynamic performance. The first group of direct tests mentioned above is directed primarily toward the evaluation of these engineering properties. The indirect tests offer a basis for inference with respect to the mechanical properties. In all cases, the trends are qualitatively in the same direction, but the quantitative results may vary greatly. Effects of temperature and time are

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progressive, and depend on the extremes to which the exposure is carried. On the basis of all the tests conducted to date, the progression seems to develop first with an increase in hysteresis, secondly with an increase in modulus, and thirdly with the embrittlement of the structure by crystallization.

METHODS OF TESTING FOR FREEZE RESISTANCE

Method I.—As a method for determining combined sulfur in rubber vulcanizates, the T-50 test[2,4] is well known. A modified technique has been used in the

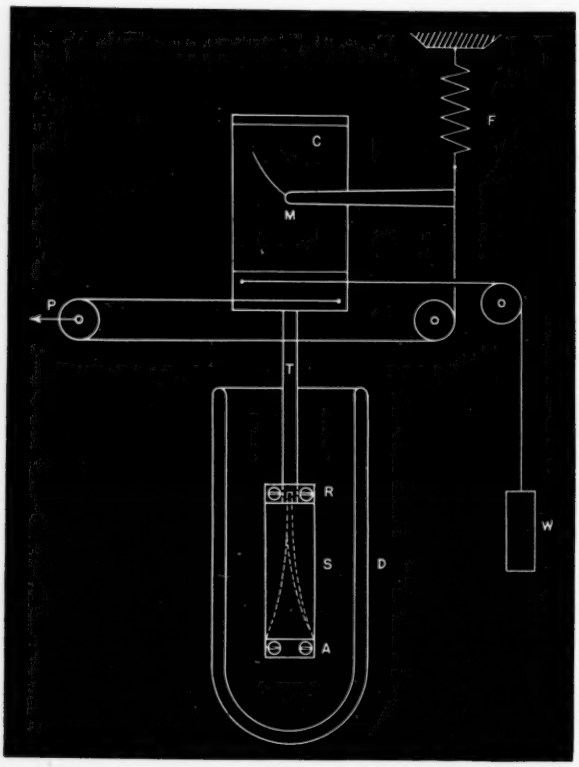

FIG. 1.—Diagram of autographic apparatus.

du Pont laboratories for the evaluation of freeze-resistance. Denatured alcohol is employed in preference to acetone as the cooling medium, since the former has less effect on the freezing and thawing of samples immersed in it.

Standard 2-inch T-50 test-specimens are used. They are racked at approximately 75 per cent of the ultimate elongation, and slowly cooled in an alcohol bath from room temperature to −70° C for about an hour. Cooling is regulated at a rate of 5 minutes per 10° C decrease in temperature to −30° C, and of 10 minutes per 10° C decrease from −30° to −70° C. At the end of the cooling period the lower ends of the specimens are released, and the temperature of the alcohol bath is raised at a rate of 1° C per minute.

The entire process of retraction is recorded, beginning with the temperature at which 10 per cent of the original elongation is recovered, and proceeding

with 10 per cent intervals of retraction until 90 per cent is recovered. In this work an extension of 170 per cent was adopted to permit the testing of compounds containing substantial quantities of carbon black, which are prone to break during the test if higher elongations are used.

The precision of the T-50 point for rubber results from its relative position on the retraction curve. Generally it lies on that part of the curve for which a slight temperature rise causes pronounced retraction. This increases the precision of the T-50 reading in the case of rubber vulcanizates. The rate of retraction of Neoprene vulcanizates at the T-50 point is much less rapid for slight changes in temperature and, for this reason, the T-50 measurement is both less precise and less significant. In testing Neoprene and other synthetic elastomers in the T-50 apparatus, it is therefore important to observe the entire retraction curve for clues to the possible behavior at low temperatures.

The T-50 test is complicated by the fact that the crystalline to amorphous transformation occurs in specimens which are stretched to an extreme in comparison with the deformations encountered in service. In addition, the results are obtained on a specimen that is thawing rather than freezing, and the specimen is in contact with a fluid which may alter the thawing characteristics. It cannot be denied that the possibility exists of a reasonable correlation between the transitions occurring in the stretched condition and those in the relatively unstretched condition. It should be kept in mind, however, that this is an assumption to avoid erroneous conclusions for materials which may not demonstrate this correlation. The test is convenient with respect to the availability of apparatus in rubber laboratories, and is very economical of test material. Although the time required to run one test is fairly lengthy, several specimens may be tested at one time.

Method II.—After a survey of the various possibilities in mechanical loading, a torsional test seemed to offer the most promise of yielding definite results with a minimum expense for apparatus. Accordingly, the autographic apparatus (Figure 1) was constructed. Test specimen S is a strip, $1 \times 3 \times 0.075$ inch, held taut between clamps A and R. The construction is such that clamp A is held stationary, while clamp R is rotated by shaft T twisting the upper end of the specimen. Chart C rotates on a drum mounted on the upper end of shaft T. A cord, wound around the drum, passes over the pulley and supports a counterbalancing 2-pound weight, W. A second cord, wound around the drum in the opposite direction, passes over the movable pulley, P, then over a second pulley to the lower end of a calibrated spring, F. A pen arm mounted on the lower end of the spring carries the marking pen, M. The clamps and test-specimen are immersed in the Dewar flask, D, of the T-50 apparatus. The upper end of the specimen is twisted through 90° (shown by the dotted lines) by pulling P in the direction shown by the arrow. This causes the autographic plotting of torque against angle of twist on chart C. By slowly releasing pulley P, an unloading curve is obtained. Experience proved that acetone and, to a lesser extent, alcohol in contact with the sample modified the freezing characteristics appreciably. Consequently, a well (not shown in Figure 1) was developed to permit the tests to be conducted in air cooled by the surrounding acetone in the Dewar flask. The time lag through the air in the well is a factor to be recognized in these tests. The curves obtained after 5-, 10-, and 15-minute immersion of a Neoprene, Type GN, "pure gum type" vulcanizate are shown in Figure 2. No fully acceptable means of expressing the results have been found, and some of them are so much at variance with the results of other experiments that the test must be considered im-

practical in its present form. On the other hand, useful preliminary work on freeze-depressants (freeze-resistant softeners) was completed in this apparatus.

Method III.—This test employes the Shore durometer used in a cold box (Figure 3). The specimen holder is an aluminum cylinder, counterbored at points on its circumference to hold $\frac{1}{2}$-inch test-specimens, $\frac{3}{4}$ inch in diameter. The cylinder may be rotated by a hand wheel on the outside of the box to bring the specimens successively under the durometer point. The durometer is actuated by a 2-pound weight mounted as shown. The durometer is drawn away from the specimens by pulling on a string passing through the wall of the cold box. The cold box is equipped with a triple glass window through which the readings may be observed without opening the box.

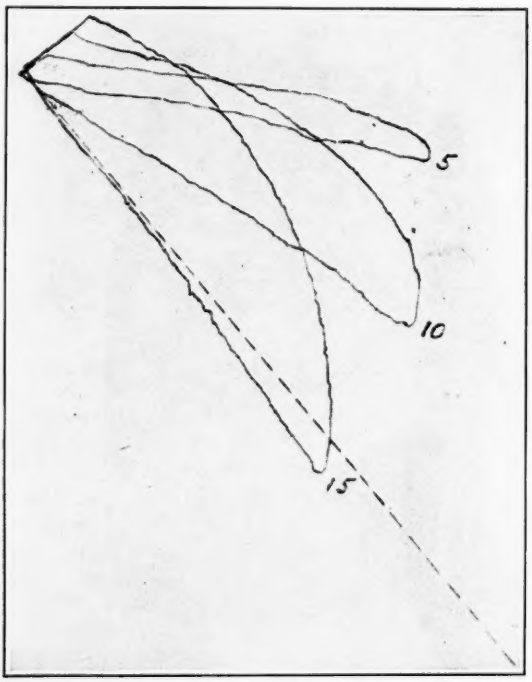

FIG. 2.—Unloading curves for Neoprene type GN after 5-, 10-, and 15-minute immersion.

The method consists of the measurement of freezing as indicated by the increase in hardness of specimens exposed to subzero temperatures for varying periods. The end point (when the sample is completely frozen) is considered to be when the vulcanizate has reached a hardness of 100 (Shore). Because of the sluggishness of all specimens after exposure to subzero temperatures, certain considerations are necessary when the hardness is determined. When the durometer is first brought into contact with the specimen, an initial deflection of the needle occurs, but it rapidly drifts to a final position. The high initial reading is considered to be due, in part, to loss of resilience caused by freezing; the final reading indicates the increase in modulus, and may be considered as the frozen hardness of the vulcanizate.

To make a comparison on an equitable basis of the freezing rates of vulcanizates

with various original hardnesses, the results are expressed as freezing factor, which is the ratio of the actual increase in hardness to the maximum possible increase (100 Shore).

$$\text{Freezing factor} = \frac{\text{hardness observed in cold box} - \text{hardness at room temp.}}{100 - \text{hardness at room temperature}} \times 100$$

Thus, the freezing factor of a pellet having a hardness of 65 at room temperature, which increased in the cold box to a hardness of 79, would be:

$$\frac{79-65}{100-65} \times 100 = 40$$

In recording the results, the freezing factor based on the true frozen hardness is expressed as a whole number, followed (in parentheses) by the freezing factor based on the initial deflection of the durometer, which includes loss in resilience of the specimen.

Generally the cold box is operated at a temperature of −34.4° or −37.2° C (−30° or −35° F), and durometer readings are taken after 1, 2, 4, 6, 24, and 48 hours. The hardness usually increases rapidly during the first 5 hours and then at a much lower rate. To condense the data, the values reported here are the freezing factor after 10 hours at the stipulated temperature. The 10-hour figure is obtained by interpolation of the readings at the time intervals stated above.

Occasionally a negative freezing factor is reported. This is due to discrepancies between hardness determinations at room temperature and in the cold box. Variations in hardness measurements by the Shore durometer are the subject of much controversy, and have not been completely eliminated in this test.

This method is considered to give results more closely related to fundamental design problems than the other methods. In addition, the apparatus takes little of an operator's time. The specimens are small, and may be used for resilience, compression set and other tests after the freezing test has been completed.

Several other methods have been advanced recently McCortney and Hendrick[6] described a test which involves a vacuum diaphragm assembly. The vacuum, expressed in mm. of mercury necessary to operate the diaphragm at room temperature, is first determined. The increase in vacuum necessary for operation after exposure to cold conditions is taken as a measure of the freezing of the diaphragm material. This method is excellent for the comparison of such automotive parts, and is a direct method in that stiffening due to cold exposure is directly measured. However, the diaphragm used in the test must be specially moulded, and changes in mould design may lead to entirely different quantitative results for a given material.

A method devised by Koch[5] measures the loss in rigidity of a frozen, bar-shaped specimen as the temperature is increased. This method appears to be well adapted to the use of very small specimens.

Several laboratories have used a method which consists of manually determining the stiffness of thin specimens after exposure to cold. Such a method is suitable, provided due consideration is given to some of the variables. The conduction of heat from the fingers to the specimen, even if only momentary contact is made, may be enough to result in a false classification of a specimen. The flexibility index must be determined with one trial, since one flex may be enough to thaw the sample partially.

The practical use of the modified T-50 etchnique (method I) and the durometer hardness method (method III) are demonstrated in the following experimental work.

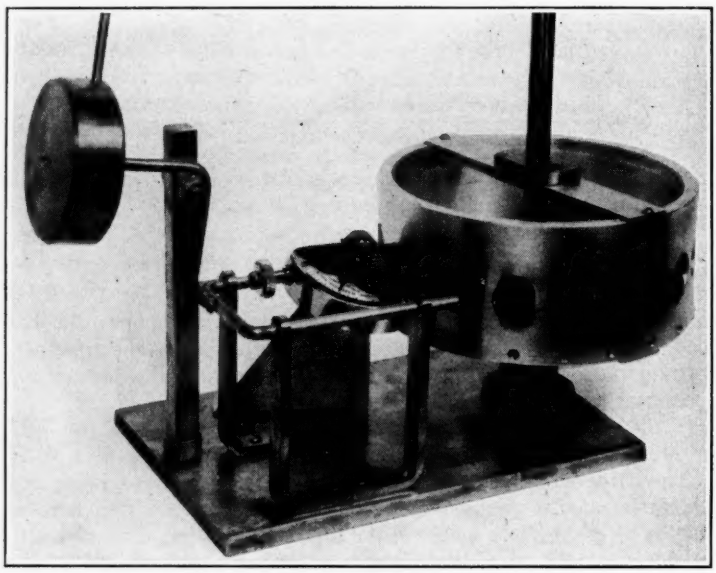

FIG. 3.—Arrangement of apparatus using the Shore durometer in a cold box

TABLE 1

COMPOSITION OF VULCANIZATES

Neoprene Type FR	100	100	100	100	—	—
Neoprene Type GN	—	—	—	—	100	—
Smoked sheet rubber	—	—	—	—	—	100
Hexamethyleneammonium hexamethylenedithiocarbamate [a]	—	—	—	—	0.1	—
Stearic acid	0.5	0.5	0.5	0.5	0.5	1.5
Phenyl-α-naphthylamine [b]	2	2	2	2	2	1.5
Extra-light calcined magnesia	—	—	—	—	4	—
Soft carbon black [c]	106	106	106	106	100	136
Petroleum-derived process oil	5	5	5	5	5	5
Sulfur	—	0.5	1	4	—	2.5
Zinc oxide	—	—	—	—	5	5
Litharge	15	15	15	15	—	—
Tetramethylthiuram monosulfide [d]	—	—	—	—	—	0.4
Press cure, min. at 141.7° C. (287° F.)	20	20	20	20	30	15

[a] Plasticizer (Latac). [b] Antioxidant (Neozone A). [c] Thermax. [d] Accelerator (Thionex).

FREEZE RESISTANCE OF RUBBER AND NEOPRENE VULCANIZATES

Natural rubber vulcanizates are more freeze-resistant than similar vulcanizates of commercial synthetic elastomers. Recently, however, a new type of oil-resistant Neoprene, *viz.*, Type FR, was developed; its vulcanizates are more freeze-resistant and have higher resilience and lower compression set than those of other synthetic elastomers. In these respects Neoprene Typre FR vulcanizates are generally equal, and frequently superior, to comparable rubber vulcanizates.

The Neoprene and rubber compounds investigated are listed in Table I. They all contained the same volume loading of carbon black.

The freeze-resistance of the vulcanizates was determined by the durometer

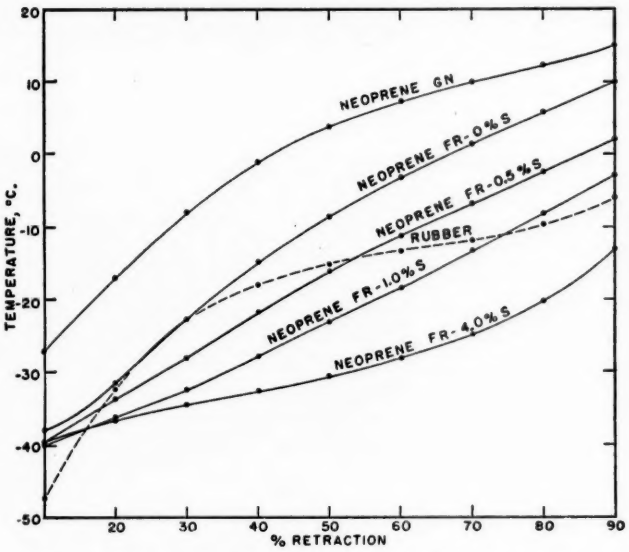

FIG. 4.—Freeze resistance of elastomers by modified T-50 technique.
(Cured 20 minutes, racked at 170 per cent elongation)

method at −37.2° C (−35° F), and the interpolated 10-hour figures are reported as follows:

Composition	Original hardness	Freezing factor
Neoprene Type FR		
0.0% sulfur	54	37 (81)
0.5% sulfur	62	35 (80)
1.0% sulfur	66	32 (79)
4.0% sulfur	74	28 (72)
Neoprene Type GN	68	77 (93)
Rubber	68	10 (80)

Figure 4 gives the retraction curves of these vulcanizates determined by the modified T-50 technique (method I). Table I and Figure 4 show that the proportion of sulfur in the Neoprene Type FR vulcanizates has a profound influence on the freeze-resistance. This is contrary to the case of other types of Neoprene, in which the presence of sulfur and sulfur-bearing materials detract from the freeze resistance. According to the modified T-50 technique, two of the Neoprene specimens appear to have better freeze resistance than the rubber vulcanizate; by the durometer method the rubber vulcanizate is superior to all the Neoprene vulcanizates, although some of the Type FR vulcanizates do not suffer so great a loss in resilience owing to the low temperature. Unreported data indicate that undercures and extreme overcures impair freeze-resistance, but these extremes should not be encountered in industrial practice.

EFFECTS OF SOFTENERS ON FREEZE RESISTANCE

The liberal use of selected softeners is to be recommended in the compounding of freeze-resistant vulcanizates. The selection of the softener usually depends on availability, price, and effectiveness, in that order. An attempt was made to

TABLE II

EFFECT OF CHEMICAL CONSTITUTION ON FREEZE RESISTANCE

Softener	Original hardness	Freezing factor
None	65	13 (77)
Aliphatic monoesters (acid radical varying)		
Butyl butyrate	—60	—5 (45)
Butyl stearate	56	36 (80)
Aliphatic diesters		
Acid radical varying		
Dibutyl adipate	59	—2 (56)
Dibutyl sebacate	58	1 (60)
Alcohol radical varying		
Dimethyl adipate	59	—1 (67)
Diethyl adipate	59	—6 (52)
Dibutyl adipate	59	—2 (56)
Diisobutyl adipate	58	—2 (65)
Dicyclohexyl adipate	58	10 (76)
Didodecyl adipate	57	51 (87)
Alkyl and aryl aromatic diesters (alcohol radical varying)		
Diethyl phthalate	59	10 (76)
Dibutyl phthalate	59	2 (71)
Dioctyl phthalate	58	2 (67)
Dicapryl phthalate	57	10 (79)
Diphenyl phthalate	58	40 (96)
Ethers and ketones		
Butylphenyl ether	59	9 (79)
Diphenyl ether	57	9 (77)
Dibenzyl ether	58	4 (62)
Diisobutyl ketone	58	15 (87)
Glycol ethers		
Methylethyleneglycol ether	65	18 (83)
Butylethyleneglycol ether	62	8 (70)
Ethyldiethyleneglycol ether	64	6 (73)
Butyldiethyleneglycol ether	61	10 (77)
Miscellaneous		
Triethyl phosphate	62	8 (81)
Tri-o-tolyl phosphate	58	22 (79)
Butylacetyl ricinoleate	55	9 (75)
Tetrachlorodipropyl ether	59	—2 (53)
Trichlorobutane	61	11 (87)
Chlorinated paraffin (60% chlorine)	59	38 (89)
Chlorinated diphenyl	58	17 (81)
Petroleum-derived process oil	57	1 (74)
Coal tar-derived process oil	57	0 (70)

TABLE III

EFFECT OF PETROLEUM DERIVATIVES ON FREEZE RESISTANCE

Material	Aniline point [a] (° F)	Saybolt universal viscosity (100° F), (sec.)	Freezing factor
Process oil	159	155.6	1 (74)
Hydraulic oil [b]	194	93.9	5 (71)
Kerosene	147	32.0	7 (72)
SAE lubricating oil No. 20	172	477.5	8 (73)
	192.5	313.3	15 (83)
	243.5	360.0	15 (81)

[a] Modified du Pont method.
[b] A commercial oil of high viscosity index, compounded with polyisobutylene.

survey systematically the field of commercially available pure chemical plasticizers and to investigate the effect of the chemical constitution of these materials on freeze-resistance. The following base compound was used:

Neoprene Type FR	100
Extra-light calcined magnesia	4
Phenyl-α-naphthylamine	2
Soft carbon black	35
Channel black	15
Sulfur	1
Zinc oxide	5
	162

To 162 grams of this compound were added 10 grams of softener, and the resulting compound was press-cured 20 minutes at 152.8° C (307° F). The softeners used and the results obtained by the durometer method, expressed as freezing after 10 hours at −30° F, are shown in Table II. As a measure of softener efficiency, the original hardness of the vulcanizates is shown.

The best class of pure chemicals of those studied as freeze-resistant softeners are the esters. As the molecular weight of like softeners in a series increases, the resistance of the vulcanizate to freezing decreases, although the ester (or esters) of lowest molecular weights may be slightly inferior to those of intermediate molecular weight. As a class butyl esters are probably to be preferred because of availability and because the boiling points are sufficiently high to prevent loss by volatilization on the mill and porosity during vulcanization. Dibutyl adipate, sebacate, and phthalate are three excellent freeze-resistant softeners. However, in freeze-resistance these esters have little, if any, superiority to the much cheaper coal tar- and petroleum-derived process oils. Aryl esters of aliphatic or aromatic acids are less freeze-resistant than alkyl esters of these acids. This fact is particularly demonstrated by the difference in dibutyl phthalate and diphenyl phthalate, which are widely used on a commercial scale as plasticizers.

In an endeavor to ascertain the effect of viscosity and(or) constitution of softeners on freeze-resistance, a range of petroleum products was examined in the same manner and by the same method as was used in the case of pure chemical softeners. The results are shown in Table III.

Obviously, with the small number of samples used, no correlation can be made between freeze-resistance and viscosity, or freeze-resistance and constitution as indicated by the aniline point. However, in a given class of petroleum products some correlation might be drawn, and it would be expected that low viscosity (with as high a viscosity index as possible) and low aniline point would favor freeze-resistance.

CONCLUSIONS

Realizing the need for general agreement throughout the rubber industry on the evaluation of the freeze-resistance of various elastomers, we have outlined several procedures and reported typical test results. Although the procedures described are inadequate as standard tests for complete evaluation, it is hoped that they may stimulate development of procedures which will be generally acceptable.

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SOLUBILITY OF POLYBUTENE IN PURE SOLVENTS *

H. C. EVANS and D. W. YOUNG

STANDARD OIL COMPANY OF NEW JERSEY, ELIZABETH, N. J.

During the past few years interest in the preparation and properties of long-chain polymers has been intensified because of their importance in the manufacture of improved petroleum products, plastics, and chemical-resistant paints. Materials such as polybutene and rubber form solutions, the viscosities of which increase rapidly with concentration. Typical viscosity-concentration data on dilute solutions of polybutene have been published[7].

A number of workers have determined the viscosities of several polymers in dilute solutions, and from these investigations equations have been proposed for expressing viscosity as a function of molecular constitution. One of the most important considerations has been the question whether very high polymeric substances exist in solution as long macromolecules, completely dispersed, or as aggregations of much shorter molecules associated in the micellar state.

Staudinger[5], one of the chief proponents of the former view, carried out a large amount of work on the viscosity of solutions of such linear polymers. His conclusions regarding chain length were based almost entirely on such measurements interpreted on the basis of the viscosity relation:

$$\eta_{sp}/c_{gm} = K_n M \tag{1}$$

$$\eta_{sp}/c = K_m P \tag{1A}$$

or

where η_{sp} = specific viscosity = relative viscosity, $\eta_r - 1$
c_{gm} = concentration of recurring unit (mole per liter)
M = molecular weight
c = concentration of polymer (grams per liter)
P = polymerization grade

Many attempts[5] were made to use the difference between the observed and calculated values of Staudinger's K constant as a measure of the solvation of polymer in solution. The results are not always reliable, however, because in some cases the particles are proposed by Staudinger to be present in solution in a structural form other than rigid, randomly kinked rods. Staudinger[5] and a number of other workers reported deviations from Equation (1) in the region of "dilute" solutions.

As an example of this effect, it has been demonstrated that polyvinyl chloride in dioxane does not give a straight line when the η_{sp}/c value is plotted against molecular weight. Polyvinyl chloride with a polymerization number of 1000 had about the same η_{sp}/c value as a polyvinyl chloride with a polymerization number of about 2500. This fact has been explained on the assumption that the molecules are not extended in dioxane.

Staudinger assumed that solvents which do not allow the polymeric molecules to be extended as long threads are poor solvents. Also, Lovell and Hibbert[4] deter-

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mined the viscosities of polyoxyethyleneglycol in dioxane and carbon tetrachloride. By the use of Huggins' theoretical equation[2] of the viscosity of chain molecules in solution, Lovell and Hibbert stated that the polyoxyethylene chain appears to be highly convoluted in solution.

Reports have been written covering the physical and chemical properties of polybutene, and solvents and nonsolvents of the polymer listed, but no attempt has been made to study the degree of solvation. At some solvent-polybutene concentrations we have already observed considerable instability of mixtures where viscosity determinations were erratic.

It was known that the viscosities of polybutene solvent blends in higher concentrations do not obey any concentration-viscosity law which might be applied for blending purposes. Several workers have observed very large viscosity-temperature effects for some blends, which do not bear out for other solvents, or even for the same solvent in other concentrations.

In view of the viscosity data published on polyvinyl chloride, polyoxyethyleneglycols, and polybutene, an investigation was initiated to study the degree of solubility of the polymer polybutene. It was hoped that information could be obtained to indicate if the thickening power of polybutene is due to shape of molecule, solvent, or solvent capacity.

METHOD OF SOLUBILITY DETERMINATION

At the beginning of the work it was felt that if "true solutions" were formed by polybutene-solvent blends, they should obey the well-known approximate relation given in Equation (2), and that any deviation from this equation should indicate the presence of insoluble polymer and the formation of a semi-stable solution. Later it was found that this is merely an empirical equation which holds approximately in a number of cases. Deviations are always observed, but, lacking a better equation for the wide range of concentration studied, we have used this relation as an arbitrary standard to observe variations in the thickening power of the polymer:

$$\frac{\text{log relative viscosity}}{\text{concentration}} = \text{constant} \qquad (2)$$

It was known that electroviscous effects[6], particle shape, etc., could operate in causing the viscosity to differ from the calculated viscosity. Therefore, viscosity measurements do not give a true picture of polybutene solubility.

As a check on solvent power as indicated by viscosity, an alcohol precipitation procedure was used to study the stability of solutions. A solution that requires a large amount of low-molecular-weight alcohol or nonsolvent before the polybutene is precipitated indicates qualitatively a better solvent than a solution that requires a small volume of alcohol.

Erbring[1] found it advantageous to study the interaction between solvent and substance to be dissolved, not only from a chemical structure viewpoint, but also with consideration of physical data, such as dielectric constants. He found that the amount of alcohol necessary to precipitate polybutene in solutuion was proportional to the dielectric constant of the alcohol.

Erbring[1] reported an alcohol precipitation method for the comparison of the solubility of high-molecular compounds in solvents. This procedure was used to study the stability of polybutene solutions. The method makes it possible to list solvents in order of their capability of being blended with alcohol by the use of "alcohol number". The procedure is based on the fact that alcohol precipitates

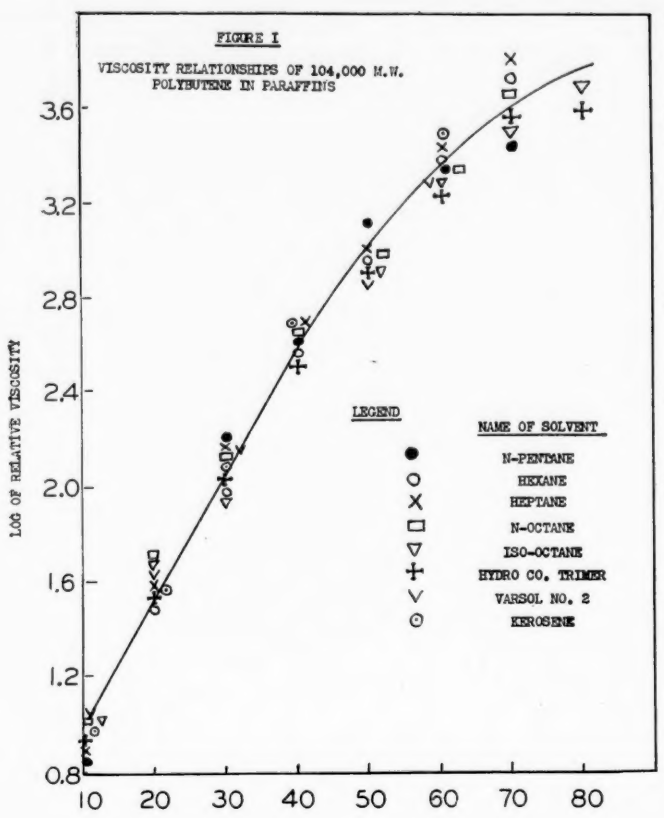
FIGURE I
VISCOSITY RELATIONSHIPS OF 104,000 M.W. POLYBUTENE IN PARAFFINS
LOG OF RELATIVE VISCOSITY
LEGEND
NAME OF SOLVENT
N-PENTANE
HEXANE
HEPTANE
N-OCTANE
ISO-OCTANE
HYDRO CO. TRIMER
VARSOL NO. 2
KEROSENE
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
10
20
30
40
50
60
70
80

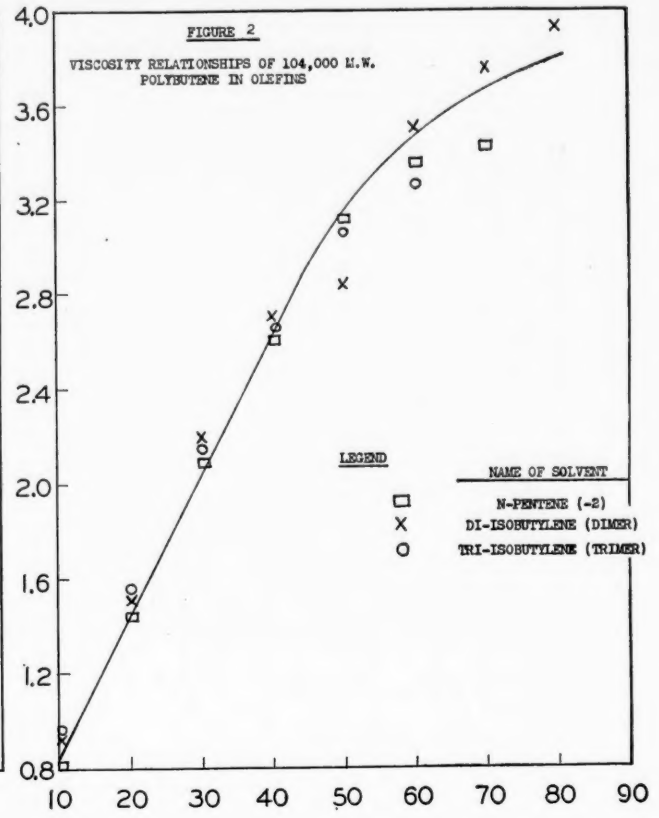
FIGURE 2
VISCOSITY RELATIONSHIPS OF 104,000 M.W. POLYBUTENE IN OLEFINS
LEGEND
NAME OF SOLVENT
N-PENTENE (-2)
DI-ISOBUTYLENE (DIMER)
TRI-ISOBUTYLENE (TRIMER)
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
4.0
10
20
30
40
50
60
70
80
90

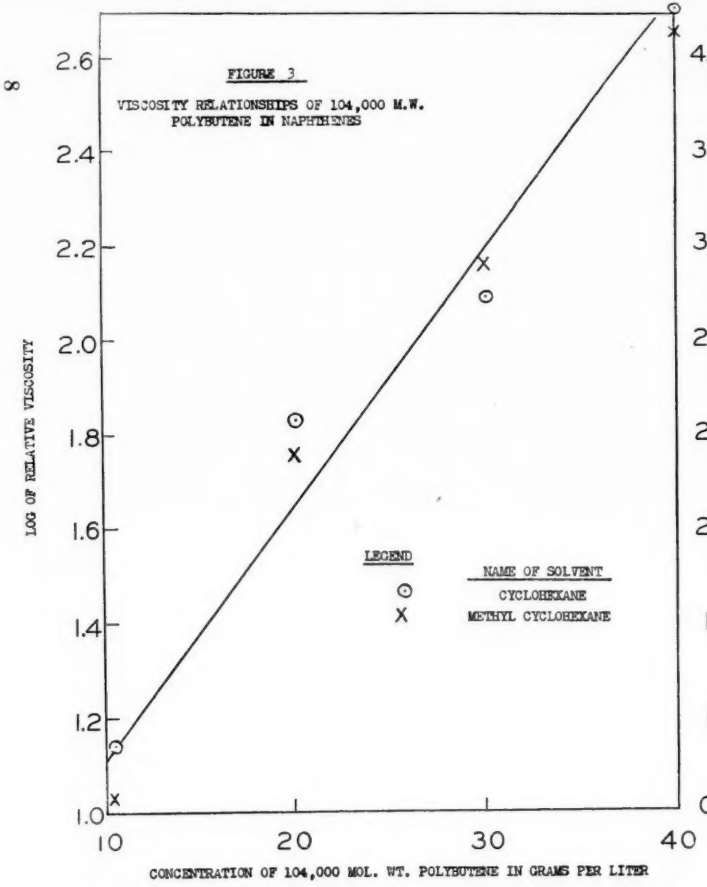
FIGURE 3
VISCOSITY RELATIONSHIPS OF 104,000 M.W. POLYBUTENE IN NAPHTHENES
LOG OF RELATIVE VISCOSITY
CONCENTRATION OF 104,000 MOL. WT. POLYBUTENE IN GRAMS PER LITER
LEGEND
NAME OF SOLVENT
CYCLOHEXANE
METHYL CYCLOHEXANE

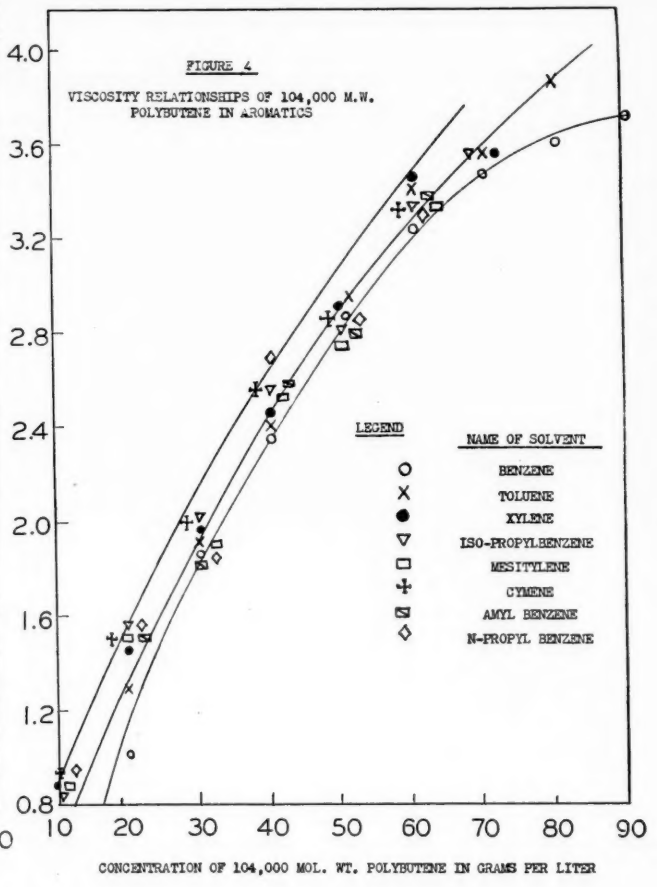
FIGURE 4
VISCOSITY RELATIONSHIPS OF 104,000 M.W. POLYBUTENE IN AROMATICS
CONCENTRATION OF 104,000 MOL. WT. POLYBUTENE IN GRAMS PER LITER
LEGEND
NAME OF SOLVENT
BENZENE
TOLUENE
XYLENE
ISO-PROPYLBENZENE
MESITYLENE
CYMENE
AMYL BENZENE
N-PROPYL BENZENE

FIGS. 1 to 4.

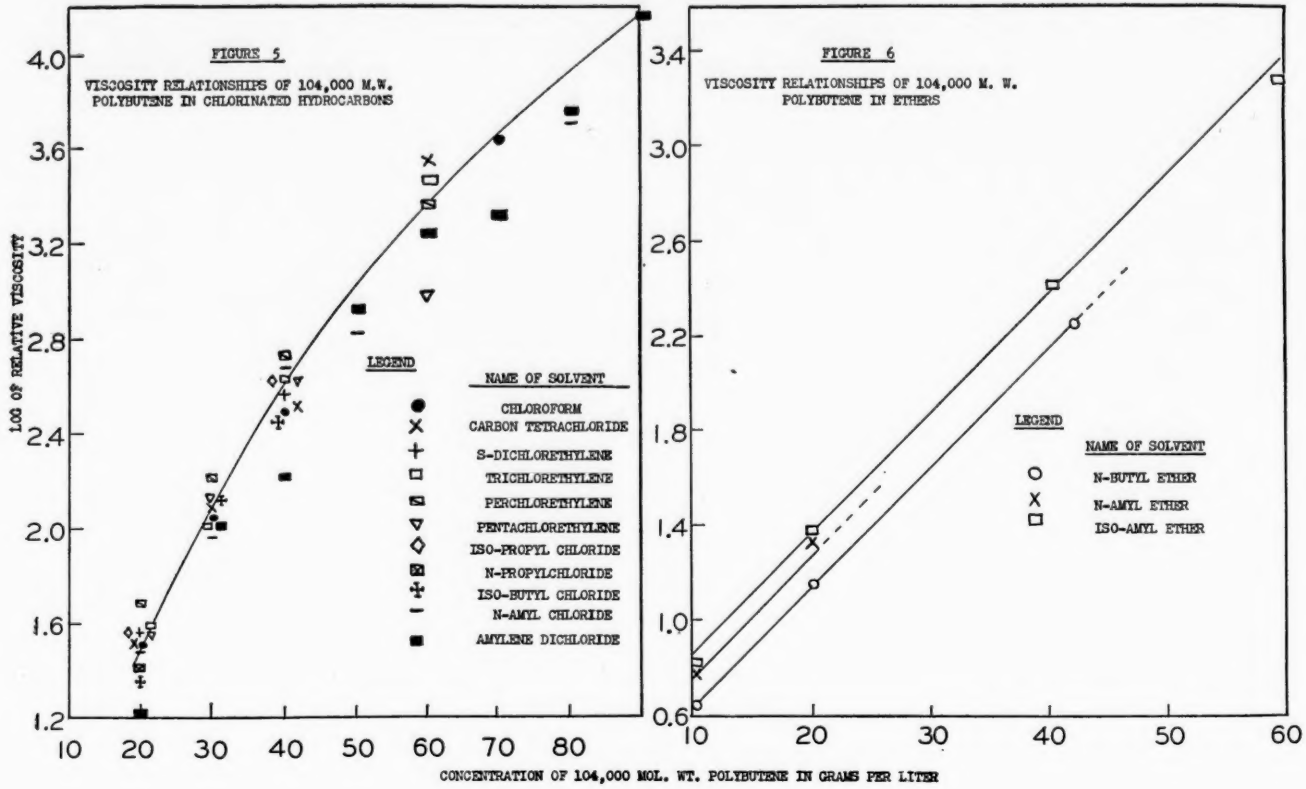
FIGURE 5
VISCOSITY RELATIONSHIPS OF 104,000 M.W. POLYBUTENE IN CHLORINATED HYDROCARBONS
LOG OF RELATIVE VISCOSITY
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
10 20 30 40 50 60 70 80
LEGEND
NAME OF SOLVENT
CHLOROFORM
CARBON TETRACHLORIDE
S-DICHLORETHYLENE
TRICHLORETHYLENE
PERCHLORETHYLENE
PENTACHLORETHYLENE
ISO-PROPYL CHLORIDE
N-PROPYLCHLORIDE
ISO-BUTYL CHLORIDE
N-AMYL CHLORIDE
AMYLENE DICHLORIDE
FIGURE 6
VISCOSITY RELATIONSHIPS OF 104,000 M. W. POLYBUTENE IN ETHERS
3.4
3.0
2.6
2.2
1.8
1.4
1.0
0.6
10 20 30 40 50 60
LEGEND
NAME OF SOLVENT
N-BUTYL ETHER
N-AMYL ETHER
ISO-AMYL ETHER
CONCENTRATION OF 104,000 MOL. WT. POLYBUTENE IN GRAMS PER LITER

Figs. 5 and 6.

polybutene from solution, and the intensity of light reflected in a nephelometer is proportional to the number of particles in suspension.

The amount of alcohol necessary varies with the temperature, dielectric constant of the alcohol and solvent, and the concentration of the solution. In this work, a blank was always titrated to determine if a cloud was produced by mixing solvent and alcohol alone. The nephelometer or cloud point method is well suited for a study of a polybutene solution of 10 grams per liter, as the colloidal precipitate formed by the action of the alcohol does not settle at room temperature at a fast rate when the relative turbidity is about 200 to 600 per cent. Erbring showed that, when the degree of relative turbidity (y axis) is plotted against the concentration of alcohol (x axis), an **S**-shaped curve is obtained. In other words, the ascent of the curve is extreme. This may indicate that polybutene precipitation takes place throughout the solution within a narrow range of concentration of alcohol.

LABORATORY PROCEDURE

Preparation of sample.—The technique of preparing polymer solutions has been found to be important, as the higher molecular weight material appears to undergo some degradation when shaken violently in solution[7]. A solution of 81,500 molecular-weight polybutene (1 gram of polymer per liter) in diisobutylene gave a viscosity of 0.973 centistoke at 20° C, but after the solution had been shaken violently for 2 hours at room temperature, the viscosity was 0.940 centistoke at 20° C. To exclude the possibility of breakdown, the present experimental solutions were made with a minimum amount of agitation.

The general procedure chosen, after some preliminary investigation, was as follows: The solution was obtained by cutting the polybutene (molecular weight 104,000) to about 0.6 cm. cube or smaller, placing the weighed sample in a 125-cc. narrow, clearglass oil bottle, and adding to this the calculated volume of solvent from a graduated buret. The total volume of polymer solution prepared was about 100 cc. As soon as the solvent had been added, the bottle was tightly corked and then placed on the laboratory desk for about 5 days. This operation permitted the polymer to soften and swell in the solvent at room temperature.

After the polymer appeared to be very soft, the "solution" or mixture was gently agitated by hand intermittently from 5 to 15 minutes a day over a period of 15 to 20 days. When the solution appeared to be uniform, the bottle was allowed to stand at room temperature.

Viscosity determination.—The viscosity was then measured on about 30-40 cc. of the solution at 37.78° C, using a Ubbelohde viscometer. The viscometers were thermostated in a water bath, and the temperature was held to an accuracy of ± 0.02° C. Timing was by a split-second precision electric timer read to ± 0.05 second.

Alcohol precipitation.—As a check or comparison on the viscosity determination, a modification of the alcohol precipitation method of Erbring[1] was used to study the stability of each polymer solution at 25° C. The general object of this test was to study the procedure of precipitation of polybutene in several solvents when alcohol was added. The precipitation was observed optically by measuring the intensity of turbidity with increasing concentrations of alcohol. All measurements were carried out with the Kober nephelometer[3]. The end points obtained were sharp, and could be reproduced within an accuracy of about 2 per cent.

Table I

Solubility Behavior of Polybutenes at Room Temperature

Solvent	Properties of solvent: Boiling point at 760 mm. (° C)	Dielectric constant E [8]	Temp. of E detn. (° C)	Av. mol. wt. of polybutene [7]	Temp. of viscosity detn. (° C)	Viscosity [a] of solutions in centistokes, at polybutene concentration of (g. per l.): 0	10	20	30	40	50	60	70	80	90	100
Paraffins																
n-Pentane	35.95	1.80	20.3	104,000	20	0.425	2.81	15.6	57.0	170	577	975	1100	—	—	—[b]
n-Hexane	68.75	1.87	20	104,000	37.78	0.438	2.61	12.4	43.4	172	433	1052	2245	—	—	—
n-Heptane	98.40	1.97	20	104,000	37.78	0.549	3.82	20.2	70.9	280	627	1382	3167	—	—	—
n-Octane	125.75	1.96	20	104,000	37.78	0.653	5.51	29.2	80.4	276	641	1498	2992	—	—	—
Isooctane	116.00	—	—	104,000	37.78	0.647	5.40	27.6	56.8	278	546	1244	1996	3092	—	—
Hydro Co. trimer	150–180	—	—	104,000	37.78	0.842	6.37	27.5	90.5	274	671	1578	2898	3251	—	—
Varsol No. 2	152–193	—	—	104,000	37.78	1.05	9.64	43.0	131.2	—	761	1970	—	—	—	—
Kerosene	190–274	—	—	104,000	37.78	1.62	13.50	58.9	189.2	779	—	4934	—	—	—	—
Olefins																
n-Pentene (—2)	36	—	—	104,000	20	0.403	2.59	11.65	54.0	162	544	951	1050	—	—	—
Dimer (diisobutylene)	102.6	—	—	104,000	37.78	0.665	5.68	25.05	105.7	312	441	2118	3581	5422	—	—
Trimer (triisobutylene)	130–170	—	—	104,000	37.78	1.20	10.38	44.74	177.5	533	1494	2260	—	—	—	—
Naphthenes																
Cyclohexane	80.8	2.05	20	104,000	37.78	0.971	13.20	64.64	122	501	—	—	—	—	—	—
Methylcyclohexane	100.8	—	—	104,000	37.78	0.808	9.54	45.60	115	372	—	—	—	—	—	—
Aromatics																
Benzene	79.6	2.28	20	104,000	37.78	0.623	2.47	13.2	53.2	145	454	1213	1780	2660	3,150	3,525[c]
Toluene	110.5	2.33	20	104,000	37.78	0.606	3.17	11.6	56.6	152	478	1543	2337	5040	—	—
Xylene	137–140	2.57	20	104,000	37.78	0.665	5.24	18.1	63.2	185	484	1752	2500	5510	—	—
Isopropylbenzene	153.4	—	—	104,000	37.78	0.771	5.58	27.4	79.3	292	490	1771	2900	—	—	—
n-Propylbenzene	157.5	2.36	20	104,000	37.78	0.844	6.66	27.9	78.4	300	514	1933	—	—	—	—
Mesitylene	164.6	2.35	20	104,000	37.78	0.703	5.55	22.7	73.5	259	440	1628	—	—	—	—
Cymene	176.0	—	—	104,000	37.78	1.00	7.89	33.2	80.0	370	627	2280	—	—	—	—
Amylbenzene	194	—	—	104,000	37.78	1.23	10.33	40.0	99.1	625	800	2700	—	—	—	—
Clorinated Hydrocarbons																
Methylene chloride	39.8	9.2	20	104,000	37.78	0.361	0.37	—	—	—	—	—	—	—	—	—[d]
Methylene chloride	39.8	9.2	20	12,000	37.78	0.361	0.53	—	—	—	—	—	—	—	—	—[e]
Chloroform	61.2	4.8	20	104,000	37.78	0.405	2.87	13.3	44.1	124.1	—	—	1759	—	—	—
Carbon tetrachloride	76.7	2.2	20	104,000	37.78	0.533	4.40	17.7	59.0	162	—	1868	—	—	—	—
s-Dichloroethylene	48.4	2.4	20	104,000	37.78	0.358	2.84	13.1	—	136	—	—	—	—	—	—
s-Dichloroethylene	60.3	9.4	20	104,000	37.78	0.400	0.40	—	—	—	—	—	—	—	—	—[f]
Mixt. of preceding two liquids	48–60	—	—	104,000	37.78	0.380	1.27	6.43	29.8	—	—	—	—	—	—	—[g]
Trichloroethylene	86.7	3.4	20	104,000	37.78	0.421	3.45	15.6	48.6	175	—	1247	—	—	—	7,461
Perchloroethylene	120.8	2.4	20	104,000	37.78	0.498	5.46	24.9	79.3	282	—	1171	—	—	—	18,555
Ethylene dichloride	83.7	10.4	20	104,000	37.78	0.573	0.57	0.57	—	—	—	—	—	—	—	—[f]
Ethylene dichloride	83.7	10.4	20	12,000	37.78	0.573	0.57	0.57	—	—	—	—	—	—	—	—[f]
β-Trichloroethane	113.5	10.0	20	104,000	37.78	0.686	0.66	0.69	—	—	—	—	—	—	—	—[f]
β-Trichloroethane	113.5	10.0	20	12,000	37.78	0.686	—[f]	—	—	—	—	—	—	—	—	—[h]

TABLE I.—*Continued*

Solvent	Properties of solvent: Boiling point at 760 mm. (° C)	Dielectric constant E [8]	Temp. of E detn. (° C)	Av. mol. wt. of polybutene [7]	Temp. of viscosity detn. (° C)	Viscosity [a] of solutions in centistokes, at polybutene concentration of (g. per l.): 0	10	20	30	40	50	60	70	80	90	100
CHLORINATED HYDROCARBONS.—Continued																
s-Tetrachloroethane	146.3	8.0	20	104,000	37.78	0.862	1.53	1.77	—	—	—	—	—	—	—	—[f]
s-Tetrachloroethane	146.3	8.0	20	12,000	37.78	0.862	1.15	1.57	—	—	—	—	—	—	—	—[i]
Pentachloroethane	161.9	3.7	20	104,000	37.78	1.14	8.72	41.7	135	478	—	1137	—	—	—	—
Isopropyl chloride	36.5	—	—	104,000	20	0.442	15.9	—	—	177	—	—	—	—	—	—[j]
n-Propyl chloride	46.5	7.7	20	104,000	37 78	0.452	—	11.3	—	—	—	—	—	—	—	—
2,2-Dichloropropane	70.5	10.2	18.8	104,000	37.78	0.623	0.623	—	—	—	—	—	—	—	—	—[f]
1,2-Dichloropropane	95.9	—	—	104,000	37.78	0.634	0.642	—	—	—	—	—	—	—	—	—[f]
Isobutyl chloride	68.0	7.1	20	104,000	37.78	0.507	3.62	12.7	58.8	154	—	—	—	—	—	—
n-Amyl chloride	105.7	6.6	11	104,000	37.78	0.587	4.21	18.3	52.2	279	381.0	—	—	3220	—	—
Amylene dichloride	130–175	—	—	104,000	37.78	0.949	5.44	15.1	66.8	152	779.0	1749	1957	5665	13,778	—
ALCOHOLS																
Methanol	64.5	30.2	25	12,000	Not detd.	—	—	—	—	—	—	—	—	—	—	—[f]
Ethanol	78.3	24.1	25	12,000	Not detd.	—	—	—	—	—	—	—	—	—	—	—[f]
n-Pentanol	137.9	13.7	25	12,000	Not detd.	—	—	—	—	—	—	—	—	—	—	—[f]
Tetradecanol	263.2	—	—	104,000	37.78	12.75	13.4	13.7	13.7	13.8	—	—	—	—	—	—[k]
Heptadecanol	309.0	—	—	104,000	37.78	21.59	28.5	31.2	44.5	46.2	48.9	—	—	—	—	—[k]
ETHERS																
Ethyl ether	34.6	4.3	20	12,000	Not detd.	—	—	—	—	—	—	—	—	—	—	—[f]
n-Butyl ether	139–141	—	—	104,000	37.78	0.766	3.39	11.12	—	124	—	—	—	—	—	—
n-Amyl ether	187–190	3.1	16	104,000	37.78	1.13	7.02	25.85	—	—	—	—	—	—	—	—
Isoamyl ether	56–58 (14 mm.)	—	—	104,000	37.78	1.04	6.83	24.90	—	262	—	2044	—	—	—	—
β,β-Dichloroethyl ether	175–179	—	—	104,000	37.78	1.40	1.40	1.40	—	—	—	—	—	—	—	—[f]
ESTERS																
Isoamyl formate	122–123	—	—	104,000	37.78	0.736	0.736	0.736	—	—	—	—	—	—	—	—[f]
Butyl acetate	118–127	—	—	104,000	37.78	0.875	0.950	—	—	—	—	—	—	—	—	—[f]
Isoamyl butyrate	159–179	—	—	104,000	37.78	0.969	1.12	1.11	1.12	1.13	1.16	1.16	1.16	1.16	1.17	1.17[f]
Isoamyl caproate	85–109 (15 mm.)	—	—	104,000	37.78	1.42	4.00	15.49	—	—	495	—	—	—	—	—[i]
Methyl oleate	189–191 (10 mm.)	—	—	104,000	37.78	7.84	8.27	9.63	12.18	15.3	15.3	16.1	16.8	16.9	17.2	17.4[k]
MISCELLANEOUS																
Mesityl oxide	128.7	15.4	20	104,000	37.78	0.642	0.643	0.643	0.643	—	—	—	—	—	—	—[f]
Solvenol No. 1	190–212	—	—	104,000	37.78	1.04	9.47	—	—	—	—	—	—	—	—	—[i]
Ethyl sulfide	91.6	7.2	20	104,000	37.78	0.502	3.49	14.3	65.1	198	680	—	—	—	—	—

[a] Viscosity determined by A. S. T. M. method D445-38T (1938). [b] Blue haze at 25° C. [c] Blue haze at 20° C. [d] Precipitate at 25° C. [e] Clear and soft at 35° C. [f] Hard precipitate at 25° C. [g] Soft precipitate. [h] Soluble at 66° C. [i] Soluble at 25° C. [j] Precipitate at 10° C, blue haze at 25° C. [k] Soft precipitate at 25° C. [l] Solid, clear gel.

VISCOSITY-CONCENTRATION RELATIONSHIP

Table I summarizes the viscosity concentration determinations on a number of solvents using, in the main, a polybutene of 104,000 molecular weight. The viscosity was determined at 37.78° C for the solvents with high boiling points and at 20° C for the solvents with relatively low boiling points.

Table I and Figures 1 to 6 illustrate the difficulty of a solubility determination from these data alone. Poor solvents, such as alcohols, esters, low molecular-weight ethers, and some chlorinated hydrocarbons, identify themselves by precipitation; the poorest of these are identified by their inertness to the polybutene itself.

TABLE II

COMPARISON OF CHANGES IN VISCOSITY OF POLYMER SOLUTIONS [a] WITH ALCOHOL NUMBER

Solvent	η_{sp}/c at 25° C	Cc. 2-Ethylbutyl alcohol to form 400% relative turbidity in 25 cc. polymer soln. at room temp.
Benzene	0.221	14.6
Toluene	0.429	20.3
Xylene	0.678	21.7
n-Propylbenzene	0.690	21.7
Mesitylene	0.690	21.8
Cymene	0.714	21.9
Amylbenzene	0.784	22.0
n-Hexane	0.530	22.9
n-Heptane	0.855	26.4
n-Octane	0.923	26.5
Varsol No. 2	1.018	31.8
Isoamyl butyrate	0.057	0.0 [b]
Isoamyl caproate	0.150	1.8

[a] Concentration of polymer (104,000 mol. wt.), 10 grams per liter.
[b] Turbid solution agitated before viscosity determination.

The slopes of the viscosity-concentration curves of some of the solvents following a general deviation from the Arrhenius equation: ($\log N = KC$), tend to drop rather suddenly in the higher concentrations, and thereby form plateaus on the curve at concentrations greater than about 50 grams per liter. We had thought it might be possible to determine the plateau for each solvent and, in this way, to classify them in order of solubility by the concentrations which could be attained before this phenomenon took place. This idea had to be revised when it was discovered that the determination of viscosities in this range was difficult with the available equipment, and the results themselves were not always reproducible.

The gradual reduction of the slope of the curves as the concentration is increased can be explained by any of the discussed theories which seek to explain the reduction of the thickening power of the polymer. As the slope of the curve approaches zero (Figures 1 to 6), the system is unstable, viscosities are susceptible to mechanical treatment (for example, it was possible to increase a 11.75 gram per liter blend of polybutene in benzene from 2.17 to 4.60 centistokes at 25° C by violent agitation), and precipitation is observed in the lower viscosity blends.

To observe the effect of solution concentration above this plateau, Figure 7 pictures the viscosities of various concentrations of polybutene in *n*-butyl ether. Above the unstable range a third system about as stable as the first is formed. It is thought that this third system may follow some plasticity law up to the

viscosity of the solid polymer. Also, for this solvent a solution with about 40 grams of polymer per liter shows a slight change in viscosity over the temperature range 20° 37.78° C.

A possible explanation for this phenomenon is that the polymer is present in poor solvents in two phases—a molecularly dispersed polymer-in-solvent phase and a mechanically dispersed solvent-in-polymer phase within the first phase. Accordingly, an increase in temperature reduces the second phase and, by increasing the first phase, increases the overall thickening effect of the polymer.

As the concentration-viscosity curves could not in themselves be used to classify the solubility of the various solvents, alcohol precipitation experiments were run on several of the 10 gram per liter solutions; these results checked with the calculated η_{sp}/c values (Table II). In a general way the results give excellent correla-

TABLE III

DEGREE OF POLYBUTENE SOLUBILITY AS DETERMINED BY η_{sp}/c VALUES [a] AT 37.78° C

	η_{sp}/c
Paraffins	
n-Hexane	0.495
n-Heptane	0.595
Hydro Co. trimer	0.656
Isooctane	0.734
Kerosene	0.734
n-Octane	0.744
Varsol No. 2	0.816
Olefins	
Dimer (diisobutylene)	0.754
Trimer (triisobutylene)	0.764
Naphthenes	
Methylcyclohexane	1.08
Cyclohexane	1.26
Aromatics	
Benzene	0.296
Toluene	0.423
Isopropylbenzene	0.624
Xylene	0.688
Cymene	0.689
Mesitylene	0.690
n-Propylbenzene	0.690
Amylbenzene	0.740
Chlorinated hydrocarbons	
Amylene dichloride	4.474
Chloroform	0.608
Isobutyl chloride	0.614
n-Amyl chloride	0.618
Pentachloroethane	0.666
s-Dichloroethylene [48]	0.694
Trichloroethylene	0.720
Carbon tetrachloride	0.726
Perchloroethylene	0.995
Ethers	
n-Butyl ether	0.342
n-Amyl ether	0.520
Isoamyl ether	0.556
Ester	
Isoamyl caproate	0.182
Miscellaneous	
Ethyl sulfide	0.596
Solvenol No. 1	0.811

[a] Viscosities determined on polymer (104,000 mol. wt.) solutions at a concentration of 10 grams per liter.

tion with observed solubilities in higher concentrations of these several solvents. For example, the data in Table II indicate that a small amount of alcohol precipitates the polymer from benzene, and the data presented graphically in Figure 4 show that the benzene-polymer solution deviates at an approximate concentration of 70 grams per liter from the Arrhenius equation. The change in slope of the lines at a concentration of 70 grams per liter is more apparent for benzene than the other aromatic solvents tested. Therefore, the calculated η_{sp}/c value was used for solubility comparison, which gives an easily determinable result for each solvent. These data are listed in Table III. The solvency of polybutene in chlorinated hydrocarbons is not too well understood. Because of the high density of these solvents, our usual method of solution could not be used, and some mechanical agitation had to be resorted to. This may be the cause of some of our viscosity inconsistency. No tests were made for possible breakdown. Data in Tables I and IV show that chlorinated paraffins with dielectric constants above about 8.0 are generally nonsolvents. This dividing line is rather sharp. As no other group of solvents had members above and below this

figure, we were unable to check the overall effect of the dielectric constant. Following Erbring's reasoning, it should be possible to forecast optimum solvent-nonsolvent ratios for low-viscosity solvent blends when the minimum dielectric constant has been determined. An illustration of the importance of the dielectric constant in solubility work is data on the isomers of dichloroethylene, which show that the isomer having a dielectric constant of 2.4 was a polybutene solvent, whereas the isomer having a constant of 9.4 was not effective.

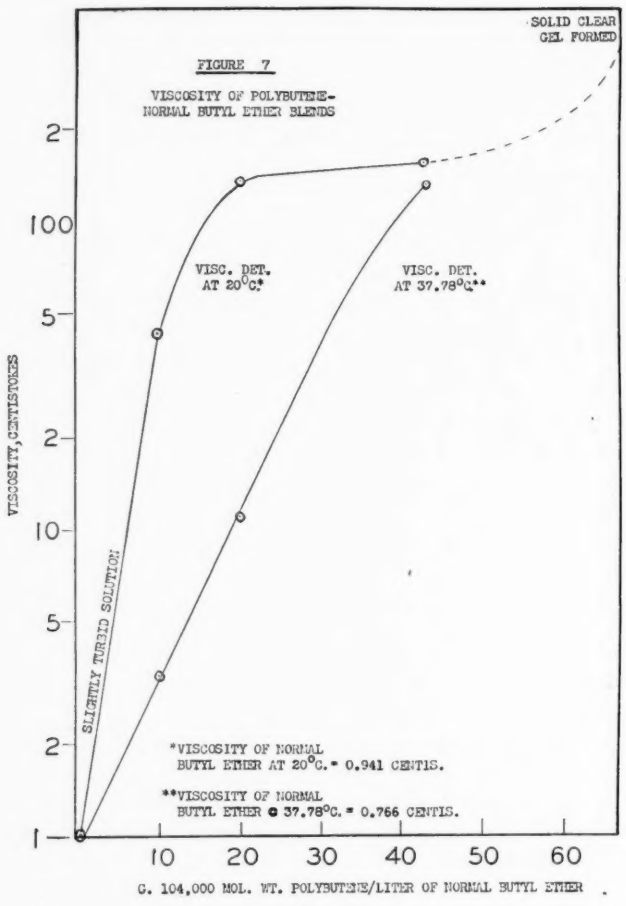

FIG. 7.

Polybutene is insoluble in the low-molecular-weight alcohols; however, as might be expected, the solubility increases as the molecular weight of the alcohol is increased. Polybutene of 12,000 molecular weight is soluble in heptadecanol as high as 100 grams per liter. Polybutene (104,000 molecular weight) increased the viscosity of heptadecanol while in contact with it, but even as low as 10 grams per liter would not completely dissolve. The latter sample, after being held in contact with heptadecanol for about 12 weeks and then separated, was analyzed to have a molecular weight of 174,000; this illustrates the fractional solvation of the medium.

TABLE IV

SOLUBILITY BEHAVIOR OF POLYBUTENE IN CHLORINATED HYDROCARBONS AT ROOM TEMPERATURE

Methylene chloride	Polymer not soluble
Chloroform	Polymer soluble
Carbon tetrachloride	Polymer soluble
s-Dichloroethylene [48]	Polymer soluble
s-Dichloroethylene [60]	Polymer not soluble
Trichloroethylene	Polymer soluble
Perchloroethylene	Polymer soluble
Ethylene dichloride	Polymer not soluble
β-Trichloroethane	Polymer not soluble
s-Tetrachloroethane	Polymer not soluble
Pentachloroethane	Polymer soluble
Isopropyl chloride	Blue haze at 25° C
n-Propyl chloride	Polymer soluble
2,2-Dichloropropane	Polymer not soluble
1,2-Dichloropropane	Polymer not soluble
Isobutyl chloride	Polymer soluble
n-Amyl chloride	Polymer soluble
Amylene dichloride	Polymer soluble

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SOLVENTS AND PLASTICIZERS FOR CHLORINATED RUBBER

CRITICAL DATA *

J. W. RAYNOLDS [1]

MELLON INSTITUTE, PITTSBURGH, PENNA.

and

M. R. RADCLIFFE and M. R. VOGEL

BINNEY AND SMITH COMPANY, EASTON, PENNA.

Halogenated rubbers have long been known, but only the chlorine derivatives have become of commercial significance. There are three fundamental modifications in which chlorine is combined with rubber hydrocarbon to form useful synthetic resins.

1. Rubber hydrochloride[4] is the reaction product of rubber and dry hydrogen chloride. The chemical reaction is one of addition, and hydrogen chloride combines at the double bonds of rubber hydrocarbon. Theoretically the chlorine content may reach a total of 34.8 per cent. Commercial products usually contain from 28.5 to 30.0 per cent combined chlorine. Rubber hydrochloride is characterized by extreme flexibility, thermoplasticity, and low solubility in a limited group of solvents, such as benzene and chloroform. The principal commercial use of this product has been in the manufacture of transparent wrapping film and sheeting.

2. Chlorinated rubber hydrochloride[3] is made by chlorination of rubber hydrochloride. By this reaction the final chlorine content may be raised to a total of about 40 per cent. Products of higher chlorine content have been reported but are not manufactured. As the chlorine content increases, the usual processes become uneconomic for commercial production.

3. Chlorinated rubber, sometimes called "rubber chloride", is the product prepared by the treatment of rubber with chlorine gas. The chemical reaction, which takes place both by addition and substitution, may continue until the final chlorine content is as much as 72 per cent. Commercial products[2] now on the market usually contain between 65 and 68 per cent chlorine, for it is within this range that the economic production of a stable product is obtained. Chlorinated rubber of 65 to 68 per cent chlorine content is soluble in a wide variety of organic solvents. It is a hard and brittle film-forming resin and, with proper treatment, may be plasticized to yield highly useful coatings for a wide variety of industrial applications. The chemical resistance of chlorinated rubber is outstanding; clear, unplasticized films have unusual resistance to aqueous acids and alkalies, alcohols, aliphatic hydrocarbons, brines, and water.

Chlorinated rubber appears to have been first prepared and described in 1859 by Englehart and Haveman[5]. For several subsequent years, a number of United States patents were granted for the manufacture and use of chlorinated rubber products, although no commercial development of any consequence took place.

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In 1917 a patent[6], issued to Peachy of Manchester, England, covered the manufacture of the heptachloro product and disclosed its use for coatings and lacquers. The heptachloro product would have a formula $C_{10}H_{13}Cl_7$ and a chlorine content of 65.13 per cent. Several years later the United Alkali Company of Great Britain began its manufacture under the trade name Duroprene, and until about 1928 it was the only chlorinated rubber on the market. During the next ten years there was a marked increase in interest in chlorinated rubbers. At least nine different brands appeared commercially in England and on the continent of Europe. During this period the first industrial manufacture in the United States was undertaken by the Hercules Powder Company; the product was known as Tornsit. This was later discontinued in favor of a new type of chlorinated rubber having improved physical properties, and known as Parlon. Earlier this year it was announced that a novel type of chorinated rubber was being placed in production, and would soon be commercially available[6]

This latest product, which will be introduced by Binney & Smith Company, is a fully saturated compound containing between 65 and 66 per cent chlorine, both added and substituted. Its chemical resistance and physical properties correspond to other chlorinated rubbers of approximately the same chlorine content. This product is Raolin, Type A.

GENERAL USE

The utilization of chlorinated rubber has been largely restricted to the formulation of chemical-resistant and concrete paints and to the fortification of alkyd-resin finishes. The new types of chlorinated rubber manufactured in the United States are reported to be very promising. They have desirable features for the following applications: moistureproof paper coatings, chemical-resistant finishes, food-container coatings, fortifiers for alkyd-resin finishes, heat-sealing paper coatings, cement, chemical-resistant paints, traffic marking paints, fire-resistant finishes or coatings, wood finishes, artificial leather dopes, printing inks, and cloth coatings.

Since solubility and broad compatibility are desirable features of a film former, chlorinated rubber is well qualified for use as such in paints, varnishes, and lacquers. It is soluble in many organic solvents, such as esters, ketones, aromatic hydrocarbons, and certain hydrogenated naphthas. Owing to its ready solubility in the latter, it lends itself well to economical formulation. Moreover, with the low-viscosity types of chlorinated rubber, high-solids lacquers may be compounded for spraying, roller coating, or other means of application, using any of the solvents mentioned. Chlorinated rubber is compatible with many of the common plasticizers and natural and synthetic resins, the properties of which are well known to paint and lacquer formulators. These three points suggest that chlorinated rubber paints and lacquers might serve in many fields now dominated by nitrocellulose and certain film-forming synthetic resins, both from the standpoint of economy and quality.

The purpose of this paper is to provide some groundwork for the formulation of chlorinated rubber finishes. The amount of fundamental data on chlorinated rubber available to the paint and lacquer formulator suffers by comparison with the wealth of information on cellulose derivatives and certain film-forming synthetic resins.

Chlorinated rubber is commercially available in a number of viscosity classifications, as measured by a 20 per cent solution in toluene. By varying the viscosity classification of the rubber chloride, a wide range of viscosity may be

obtained in any given solvent. To facilitate the adjustment of viscosity in chlorinated rubber paints and lacquers, a viscosity blending chart of the type used with nitrocellulose is of value. Such a chart is possible because the viscosity-concentration curves of chlorinated rubber in a given solvent are, for all practical purposes, straight lines, when the concentration is plotted on the plain scale and the viscosity is plotted on the logarithmic scale of a semilogarithmic graph Figure 1). By placing a straight-edge on the viscosity of *A* and on the viscosity of *B,* the percentage of each required for any intermediate viscosity is quickly determined from the bottom scale. These viscosities all refer to a 20 per cent solution in toluene.

SOLVENTS

As in the case of other paint and lacquer bases, organic liquids may be classed as either solvents or nonsolvents for rubber chloride. There is no sharp line of demarcation between the two groupings. There are solvents—for instance, acetone—which may dissolve the low-viscosity types but not those of higher viscosity. These solvents also seem to be more effective at low than at elevated temperatures. The fact remains, however, that with a given sample of chlorinated rubber, organic liquids may be divided into two groups, solvents and nonsolvents or diluents. An important effect of the solvent is the viscosity of its solution with a given viscosity classification of rubber chloride.

As previously pointed out, for all practical purposes the viscosity-concentration curve for rubber chloride in a given solvent is a straight line when plotted on semilogarithmic paper. Furthermore, the viscosity-concentration curves for a given solvent and chlorinated rubbers of various viscosities seem to have a common origin at 0 per cent concentration, which might aptly be referred to as the zero point for the particular solvent. Likewise, the curves for a rubber chloride of given viscosity and various solvents have a common point, should the curve be extrapolated, at 100 per cent chlorinated rubber. A chart with a diversity of uses has been constructed on these principles (Figure 2).

Connecting the zero point for a given solvent and the point for a given viscosity type of Raolin with a straight line gives the approximate viscosity-concentration curve of that Raolin in the particular solvent. This curve makes it possible to predetermine the viscosity for a given concentration or the concentration for a given viscosity. Extending the straight line connecting the solvent zero point and any given viscosity concentration point results in an intercept indicating the approximate viscosity type of Raolin required to produce the desired viscosity and concentration in a solution of the given solvent. Zero points for other solvents or thinner mixtures may be determined by accurately measuring the viscosity of a known solution of Raolin and extrapolating the line connecting the Raolin viscosity type and the point representing the viscosity and concentration. The intercept of this line at zero concentration is the zero point of the solvent or thinner mixture.

In the preparation of this chart, accuracy has been sacrificed for versatility. But it is thought that this fact will not detract from its usefulness because, as far as viscosities are concerned, approximations are usually all that are desired.

Where solvent power is judged from the standpoint of viscosity, it appears that the better solvents are the aromatic hydrocarbons, particularly toluene. A 20 per cent solution of a sample of rubber chloride had a viscosity of 45 centipoises in toluene; in butyl acetate the viscosity was 87 centipoises; in a mixture of butyl acetate and Lactol spirits having a dilution ratio comparable to toluene the vis-

vosity was 50 centipoises. This effect, the reduction of viscosity on the inclusion of diluents in the formula, is common to most solvent-diluent mixtures examined. Inasmuch as this case obtains, and as viscosity may be controlled by varying the viscosity type of chlorinated rubber in formulating, the implication is that a more important characteristic of the solvent may be the actual solvent strength.

The strength of a solvent may be determined by ascertaining the amount of a given nonsolvent it will tolerate while still dissolving rubber chloride. The volume of diluent tolerated by one volume of solvent expresses the dilution ratio of the solvent, this factor being a relative value for the solvent power. The solubility of chlorinated rubber in a given solvent, measured by its dilution ratio with a given nonsolvent, varies according to its viscosity classification. The higher viscosity rubber chlorides stand less dilution than those of lower viscosity. The

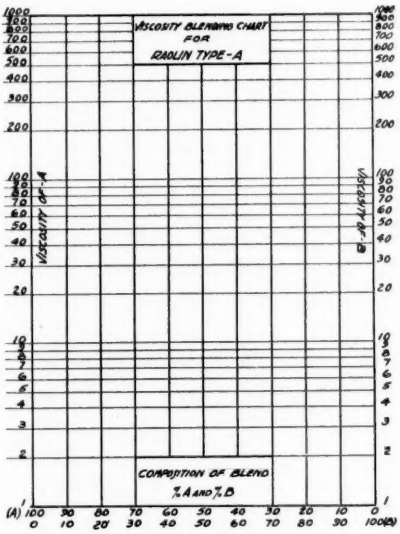

VISCOSITY BLENDING CHART
FOR
RAOLIN TYPE-A
COMPOSITION OF BLEND
% A AND % B
(A) 100 90 80 70 60 50 40 30 20 10 0
0 10 20 30 40 50 60 70 80 90 100 (B)

FIG. 1.

difference is not great. Table I shows the dilution ratios of a series of type A Raolin[6] chlorinated rubber. This effect is consistent among solvent, and amounts to about a 20 per cent variation between 5- and 1000-centipoise classifications. There is also a deviation in dilution ratio, depending on the concentration of rubber chloride in a solvent. It is surprising that the dilution ratios of the more concentrated solutions are higher. Approximately a 10 per cent variation in dilution ratio exists between concentrations of 5 and 30 per cent. In work on Raolin relating to the evaluation of solvents, the concentration has been kept constant at 10 per cent and the Raolin viscosity classification employed has been 20 centipoises, approximately the average conditions as far as dilution ratio is concerned.

Solvents for chlorinated rubber include most ester type solvents, ketones with the exemption of acetone, organic chlorides, aromatic hydrocarbons, and some hydrogenated naphthas. The relative strength of these various solvents was determined by preparing a 10 per cent solution of 20-centipose Raolin in the solvent and then titrating the solution with an aliphatic hydrocarbon cut until precipitation occurred. The volume of aliphatic hydrocarbon required to cause precipitation per volume of solvent expresses the dilution ratio. In this research, Lactol

spirits, a toluene substitute, was the aliphatic hydrocarbon fraction used. It was determined that esters and ketones are much stronger solvents for chlorinated rubber than aromatic hydrocarbons or organic chlorides. The dilution ratios of esters and ketones range between 2.0 and 2.9, whereas the dilution ratios of aromatics vary from 0.08 to 0.5 and of organic chlorides from 0.23 to 0.81 (Table II).

TABLE I

VARIATION OF DILUTION RATIO WITH VISCOSITY TYPE [a]

Toluene	Viscosity (centipoises)	Butyl acetate
0.55	5	3.15
0.52	10	3.05
0.50	20	2.88
0.45	125	2.75
0.44	1000	2.60

[a] Lactol spirits was the nonsolvent diluent used.

TABLE II

DILUTION RATIOS OF SOLVENTS FOR RUBBER CHLORIDE

Solvent	Lactol spirits dilution ratio	Solvent	Lactol spirits dilution ratio
Solvesso No. 3	0.08	Butyl lactate	2.09
Dipentene	0.10	Butyl propionate	2.12
Solvesso No. 1	0.12	Di-*n*-propyl ketone	2.22
Solvesso No. 2	0.23	Octyl acetate	2.30
Carbon tetrachloride	0.23	Amyl acetate	2.31
Hi-Flash solvent naphtha	0.26	*sec*-Butyl acetate	2.33
Xylene	0.38	Ethyl acetate	2.49
Solvesso No. 4	0.41	Methylethyl ketone	2.50
Benzene	0.49	Isobutyl acetate	2.59
Toluene	0.50	Isopropyl acetate	2.62
Dioixane	0.70	Methylisobutyl ketone	2.67
Ethylene dichloride	0.81	Cyclohexyl acetate	2.80
Cyclohexanone	1.64	*n*-Butyl acetate	2.88

DILUENTS

By a similar procedure the relative strength of nonsolvents or diluents may be determined. If a solution of rubber chloride in butyl acetate is titrated with a nonsolvent, precipitation occurs after a certain amount of the diluent has been added. The volume of diluent tolerated by one volume of butyl acetate expresses the tolerance ratio for the diluent. By observing the effectiveness of various diluents in this manner, it has been found that alcohols and acids are inferior to aliphatic hydrocarbon diluents. The tolerance ratio of alcohols range from 0.33 for ethyl to 0.84 for amyl. Acetone is an excellent diluent, as it is a borderline solvent. A broad range of tolerance ratios was obtained for various aliphatic fractions currently available to paint and lacquer manufacturers, the values falling between 2.0 and 4.7. Table III lists the values of tolerance ratios for a number of diluents.

PLASTICIZERS

The evaluation of plasticizers for chlorinated rubber is a much more complex subject than a study of solvents. The research reported here has been limited to two phases of plasticizer action: a classification of plasticizers for rubber chloride according to their solvent action, and the characterization of plasticizers by loading curves.

Plasticizers may be grouped into three more or less distinct classes: (I) a plasticizer may be an actual solvent for chlorinated rubber; (II) it may be compatible in all proportions but not a solvent; (III) its compatibility may be limited.

Owing to the fact that in plasticizers rubber chloride yields solutions of high viscosity, 10-centipoise type A Raolin was used in this phase of the work. Ten per cent solutions of chlorinated rubber in plasticizer were prepared; the solvent strength was measured by the Lactol spirits dilution ratio, the procedure being similar to the evaluation of solvents. Those plasticizers in which the chlorinated rubber did not dissolve do not belong in group I; *i.e.*, they are not active solvent plasticizers. A remarkably wide range of values was obtained in this manner, dilution ratios from 0.2 to 16.8 being found. Phthalates, sebacates, adipates, stearates, oleates, some alkyl naphthalenes, polyethers such as dicresyl Carbitol, tributyl phosphate, and certain oils may thus be classified as solvent plasticizers for Raolin (Table IV).

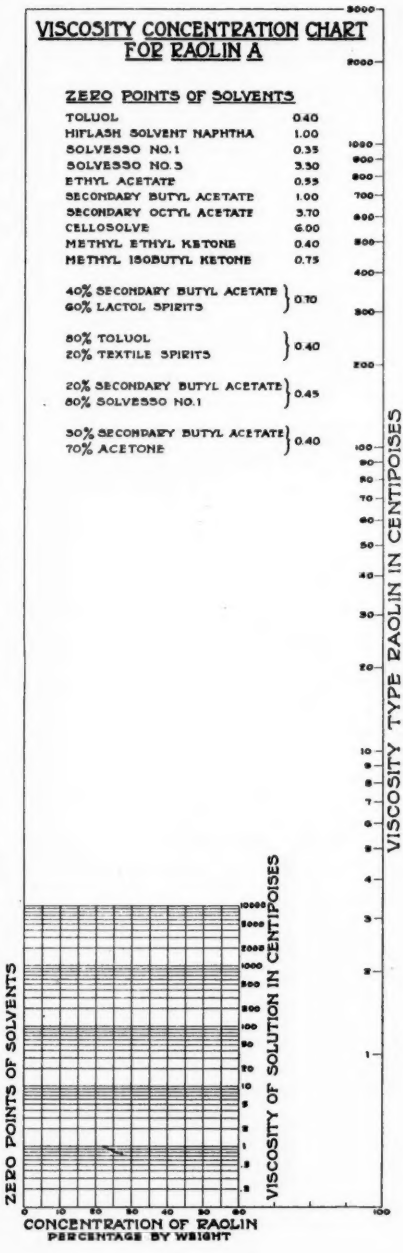

VISCOSITY CONCENTRATION CHART FOR RAOLIN A
ZERO POINTS OF SOLVENTS
TOLUOL 0.40
HIFLASH SOLVENT NAPHTHA 1.00
SOLVESSO NO.1 0.35
SOLVESSO NO.3 3.50
ETHYL ACETATE 0.55
SECONDARY BUTYL ACETATE 1.00
SECONDARY OCTYL ACETATE 3.70
CELLOSOLVE 6.00
METHYL ETHYL KETONE 0.40
METHYL ISOBUTYL KETONE 0.75
40% SECONDARY BUTYL ACETATE 60% LACTOL SPIRITS 0.70
80% TOLUOL 20% TEXTILE SPIRITS 0.40
20% SECONDARY BUTYL ACETATE 80% SOLVESSO NO.1 0.45
30% SECONDARY BUTYL ACETATE 70% ACETONE 0.40
VISCOSITY TYPE RAOLIN IN CENTIPOISES
ZERO POINTS OF SOLVENTS
VISCOSITY OF SOLUTION IN CENTIPOISES
CONCENTRATION OF RAOLIN PERCENTAGE BY WEIGHT

FIG. 2.

Those plasticizers which are nonsolvents or of limited compatibility with chlorinated rubber may be further segregated by their tolerance ratio. The tolerance ratio was determined in the same manner as for diluents—that is, by titrating a 10 per cent toluene solution of rubber chloride with the plasticizer. Some plasticizers seemed to be capable of indefinitely diluting the solution. Others showed a definite tolerance ratio, usually below 15.0. It was arbitrarily assumed that, if a plasticizer has a tolerance ratio of more than 15, it may be considered as having unlimited compatibility with rubber chloride. In this group are the

TABLE III

TOLERANCE RATIOS OF DILUENTS AND RUBBER CHLORIDE

Diluent	Tolerance ratio for 10% Raolin A in butyl acetate	% butyl acetate in 75% tolerant solution
Ethyl alcohol	0.33	80
Amyl alcohol	0.84	62
Butyl alcohol	0.86	61
Naphtha (Amsco)	2.15	38
Textile spirits	2.40	36
Kerosene	2.70	33
Kemsolene T	2.77	33
Lactol spirits	2.88	32
Gasoline (lead-free)	3.17	30
V. M. & P. naphtha	3.20	29
Acetone	3.90	25
Sunoco spirits	4.20	24
Mineral spirits	4.72	22

TABLE IV

SOLVENT PLASTICIZERS FOR RUBBER CHLORIDE (GROUP I)

Plasticizer	Lactol spirits dilution ratio	Plasticizer	Lactol spirits dilution ratio
Tributyl phosphate	16.80	Butyl stearate	1.75
Dibutyl Cellosolve phthalate	10.10	Butyl Cellosolve stearate	1.65
Diamyl phthalate	3.55	A. D. M. oil No. 100	1.50[a]
Dioctyl phthalate	3.30	Diethyleneglycol dipropionate	1.30
Dibutyl phthalate	3.10	Diglycol laurate	1.10
Tributyl citrate	2.80	Monoamyl naphthalene	0.95
Dibutyl sebacate	2.55	Di-Carbitol phthalate	0.40
Diethyl phthalate	2.40	Di-Cellosolve phthalate	0.30
Methyl Cellosolve oleate	2.25	Dimethyl Cellosolve phthalate	0.25
Methyl Cellosolveacetyl ricinoleate	2.10	Dimethyl phthalate	0.20
Butylacetyl ricinoleate	2.05	Polyamyl naphthalene	0.20
Butylphthalylbutyl glycolate	1.85		

[a] Run in the presence of a neutral solvent mixture.

bulk of the well-known plasticizers not included in group I—namely, chlorinated paraffin (42 per cent chlorine), chlorinated diphenyl (54 per cent chlorine), some alkyl naphthalenes, some ester-type plasticizers, tricresyl phosphate, most vegetable oils and their modifications, rosin derivatives, and certain nondrying oil-modified alkyd resins, as well as some liquid alkyd resins. It might be well to mention that some of these plasticizers, when warmed slightly, are solvents for chlorinated rubber (Table B).

Blown castor oil has been reported to be incompatible with chlorinated rubber in all proportions. Contrary to the findings of these previous investigators, this work has shown the film compatibility of blown castor oil to be unlimited. However, the solution compatibility of blown castor oil and chlorinated rubber depends on the strength of the solvent. With a solvent such as toluene, having a diluution ratio of 0.50, solutions of blown castor oil and chlorinated rubber are non homogeneous. Consequently the film is also nonhomogeneous. With a solvent such as butyl acetate, having a dilution ratio of 2.88, solutions containing blown castor oil and rubber chloride are clear and homogeneous, and films cast from it are perfectly clear and, in high ratios, exhibit elongation. Blown castor

oil, then, is compatible with chlorinated rubber, more so than raw castor oil which exhibits no elongation in any ratio up to 10.

This effect of the solvent on film compatibility is not limited to the case of blown castor oil. Other blown oils, such as cottonseed and certain alkyd resins, act the same way, the films from a strong solvent being clear and homogeneous, whereas films from a weak solvent are apparently incompatible. "Strength of solvent" here refers to its strength measured by dilution ratio.

In the third group of plasticizers, having limited compatibility with rubber chloride, belong those defined by a tolerance ratio of less than 15. Included in this group are fatty acids, fatty alcohols, waxes, toluene sulfonamide type plasticizers, and raw castor oil (Table VI).

TABLE V

CHLORINATED RUBBER PLASTICIZERS OF UNLIMITED COMPATIBILITY (GROUP II)

Blown castor oil [a]
Butyl *o*-benzoyl benzoate
Chlorinated diphenyls (Arochlors)
Tricresyl phosphate
Chlorinated paraffins
Diamylnaphthalene
Methylphthalylethyl glycolate
Dibutyl tartrate
Ethylphthalylethyl glycolate
Hydrogenated methl abietate
Linseed oil
Methl hexalin ester of adipic acid
Rosin oil

[a] The solution compatibility of blown castor oil depends on the strength of the solvent.

TABLE VI

CHLORINATED RUBBER PLASTICIZERS OF LIMITED COMPATIBILITY (GROUP III)

Plasticizer	Tolerance ratio of toluene solution
Castor oil	8.5
Triacetin	8.0
Toluene ethyl sulfonamide	2.5
Oleic acid	0.4

There are some interesting series among the materials examined that serve to define plasticizers for chlorinated rubber. Alkyl phthalates and their dilution ratios illustrate this point—dimethyl 0.20, diethyl 2.40, dibutyl 3.1, diamyl 3.55, and dioctyl 3.3. Results even stronger in their implication have been obtained with the phthalyl glycolates (Santicizers): methylethyl, group II, tolerance ratio 20.0; ethylethyl, group II, compatible in all proportions; butylbutyl, group I, dilution ratio 1.85.

An interpretation of these findings is that in ester plasticizers of this particular type the oxygen content has a marked effect on solvent action. There appears to be an optimum point in the solvency at an ester oxygen content of about 20 per cent. It might also be concluded that at an ester oxygen content of about 34 per cent the property of actual solvency is lost, giving way to unlimited compatibility and at still higher oxygen content resulting in limited compatibility. Another trend established in this work concerns the compatibility of alkyd resins with chlorinated rubber. Rubber chloride seems to be extremely sensitive to free hydroxyl and free carboxyl groups, as shown by the incompatibility of alcohols and acids. Observation has revealed that the lower the acid and hydroxyl numbers of alkyds, the better their compatibility with chlorinated rubber. Glycol adipate is compatible with chlorinated rubber only if it is highly esterified. Octadecanediol adipate, however, is compatible as a lower polymer, but only at com-

parable acid and hydroxyl numbers. This fact suggests the use of long-chain diols and acids in alkyds for use with chlorinated rubber. Although these comments are of a cursory nature, it is believed that they indicate trends, the knowledge of which is helpful in considerations concerning the action of plasticizers with chlorinated rubber and in the formulation of chlorinated rubber finishes.

LOADING CURVES

The second means of evaluating the effectiveness of plasticizers was the determination of loading curves which express the action of various plasticizers in softening rubber chloride films. In this work 125-centipoise Raolin type A was used. To attain comparable softening, less plasticizer was required than with lower viscosity modifications, and more was required with higher viscosity classes. The loading curves were estimated by measuring the film hardness of a series of plasticized films by the Sward rocker. Glass plates were coated with solutions of Raolin in butyl acetate at a thickness of 0.0006 inch wet and about 0.0015 inch dry; they were dried overnight at 150° F in a G. K. S. circulating-air oven and, after cooling, were tested for hardness, the average of about five determinations being the reported value. Care was exercised to be sure the films were solvent-free. Ratios of 1, 2, 4, 7, 10, and 15 parts plasticizer to 15 parts Raolin were examined. Where the hardness value is plotted against the plasticizer ratio, a curve representing the effectiveness of the plasticizer in softening the chlorinated rubber results. Not only is the ratio at which the film becomes tacky of interest, but also the general shape of the curve and its mean level. Fundamentally there are two types of curves, although some combine certain features of each of the two types.

The first type of loading curve is exemplified by dibutyl Cellosolve phathalate, a strong solvent plasticizer for chlorinated rubber (Figure 3). As a film of chlorinated rubber is plasticized with more and more of this plasticizer, the film is first softened, then hardened, and again softened. There is a maximum in the hardness curve at an intermediate plasticizer ratio, which is strange; yet the same thing occurs with other active solvent plasticizers, although perhaps not to the same marked extent.

The second type of loading curve is illustrated by chlorinated paraffin, 42 per cent chlorine (Figure 4). As the plasticizer ratio is increased, there is a consistent reduction in film hardness, a normal effect shown at least in part by most plasticizers having unlimited compatibility with rubber chloride. The degree of softening as indicated by the slope of the curve may vary considerably, however, depending on the physical properties of the plasticizer. A representative of an intermediate type of plasticizer is hydrogenated methyl abietate (Hercolyn), in which instance there is a maximum in the hardness at an intermediate ratio, coupled with a gradual and regular softening as the ratio is increased (Figure 5). Figures 6 to 20 are loading curves for a representative series of plasticizers.

One of the main points to be observed from these curves is the maximum plasticizer ratio productive of a nontacky film, which might be regarded as that point on the loading curve having a Sward hardness of 10. A second consideration would be the mean level of the curve which would represent the magnitude of the hardness resulting with the various plasticizers. Another feature is the general shape of the curve, particularly the slope. For certain purposes a gradual slope is more desirable, whereas for others a sharp drop is preferred. For instance, because a rise in temperature tends to displace the curve to the left, a plasticizer exhibiting a sharp slope would be desirable for heat-sealing

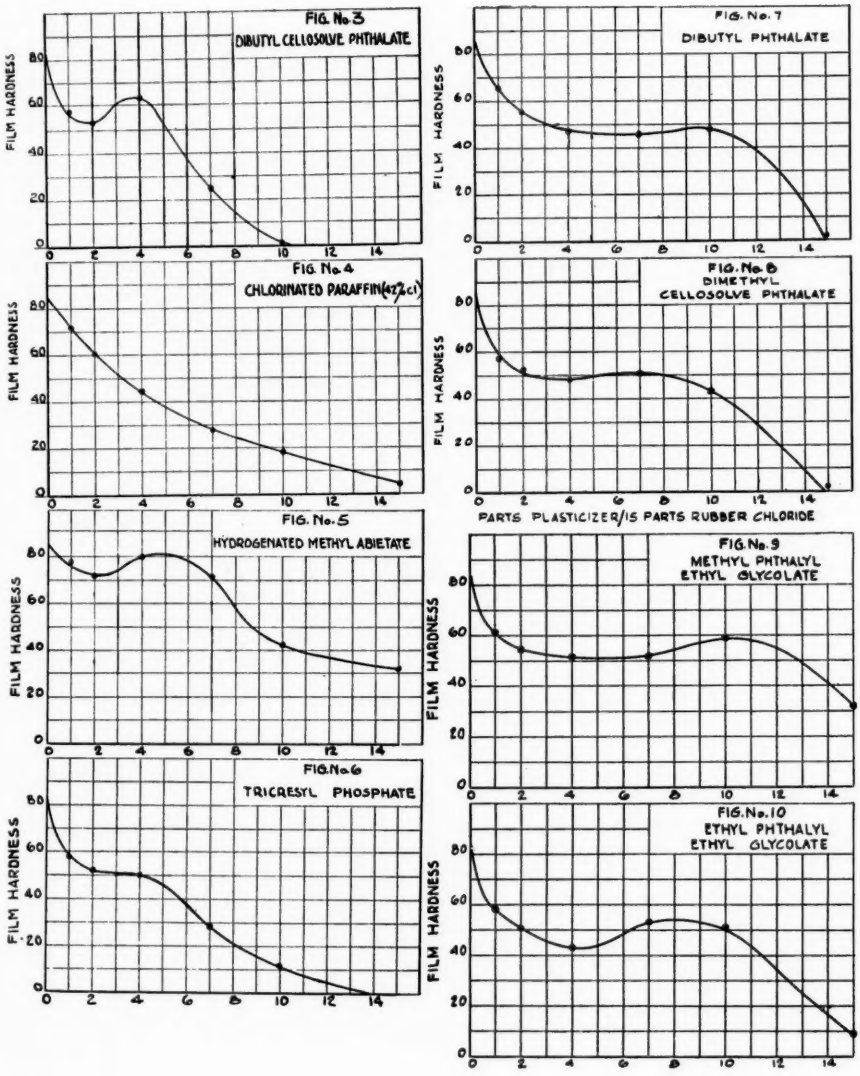


FIG. No. 3
DIBUTYL CELLOSOLVE PHTHALATE
FIG. No. 4
CHLORINATED PARAFFIN(42% Cl)
FIG. No. 5
HYDROGENATED METHYL ABIETATE
FIG. No. 6
TRICRESYL PHOSPHATE
FIG. No. 7
DIBUTYL PHTHALATE
FIG. No. 8
DIMETHYL CELLOSOLVE PHTHALATE
FIG. No. 9
METHYL PHTHALYL ETHYL GLYCOLATE
FIG. No. 10
ETHYL PHTHALYL ETHYL GLYCOLATE
FILM HARDNESS
PARTS PLASTICIZER/15 PARTS RUBBER CHLORIDE

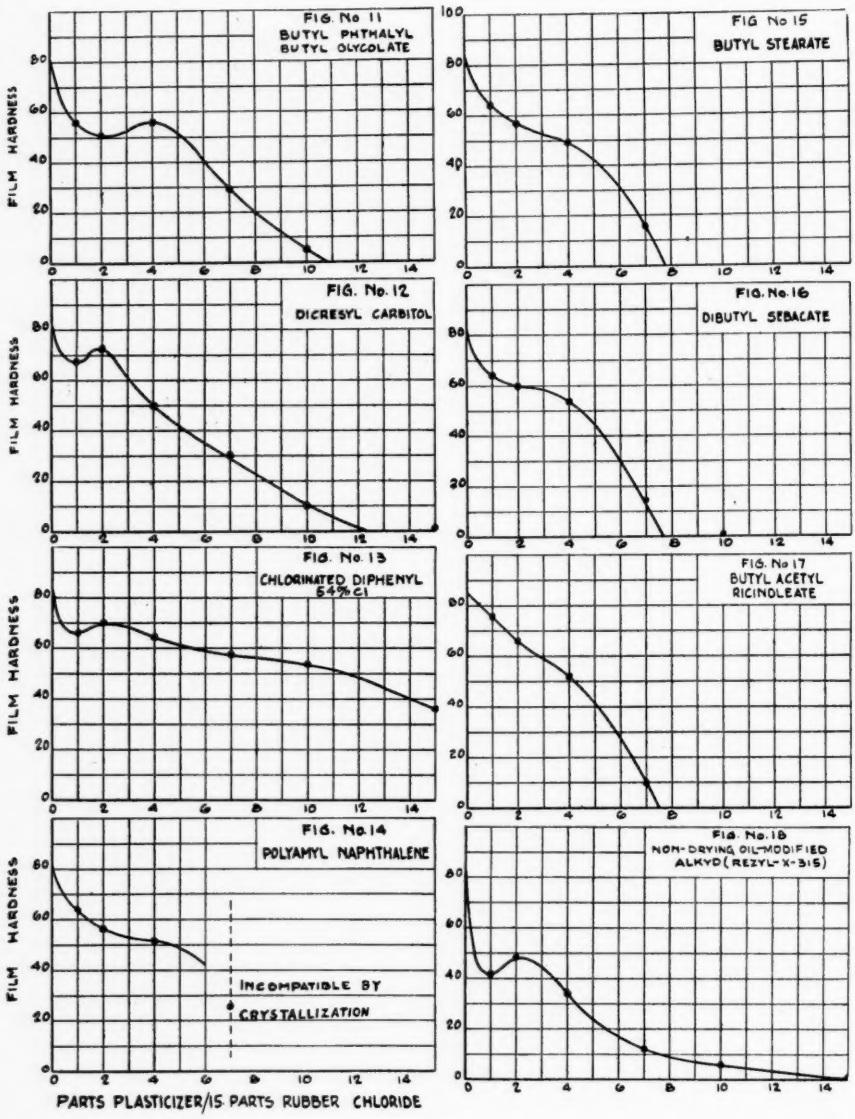


FIG. No 11
BUTYL PHTHALYL
BUTYL GLYCOLATE
FIG. No 12
DICRESYL CARBITOL
FIG. No 13
CHLORINATED DIPHENYL
54% Cl
FIG. No 14
POLYAMYL NAPHTHALENE
INCOMPATIBLE BY
CRYSTALLIZATION
FIG No 15
BUTYL STEARATE
FIG. No 16
DIBUTYL SEBACATE
FIG. No 17
BUTYL ACETYL
RICINOLEATE
FIG. No 18
NON-DRYING OIL-MODIFIED
ALKYD (REZYL-X-315)
FILM HARDNESS
PARTS PLASTICIZER/15 PARTS RUBBER CHLORIDE

and thermoplastic compositions. Conversely, where nonblocking or print resistance is desired, a plasticizer exhibiting a gradual softening would be preferable. Of course, the physical properties of the plasticizer, such as change in viscosity with temperature, complicate the predictions based on these loading curves.

Probably the most important aspect of these loading curves is the point referred to as a maximum at an intermediate ratio. In some cases this point manifests itself as an inversion in the curvature or a leveling out of the curve. It may be defined as the highest intermediate plasticizer ratio at which the continuity of the curves changes. Examination of the accompanying loading curves demonstrates that such a point exists in almost every instance. It is absent only in the case of a few plasticizers which are nonsolvent types; perhaps they might more appropriately be called "softeners", since they are effective in the same way as castor oil with nitrocellulose.

The presence of this point of discontinuity in the loading curves suggests a theory for the action of plasticizers with chlorinated rubber. There seems to be an inversion of phase at this intermediate plasticizer ratio. Expressed more

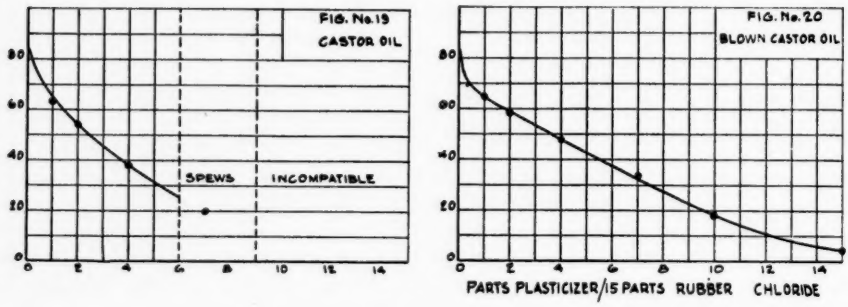
TABLE VII

ELONGATION OF PLASTICIZED RUBBER CHLORIDE FILMS

	% Elongation at ratio of:				Critical ratio from loading curves
	15/2	15/4	15/7	15/10	
Dibutyl phthalate	0	0	0	7	15/9
Arochlor-1254	0	1	15	180	15/2
Dibutyl Cellosolve phthalate	0	0	0	12	15/5
Tricresyl phosphate	0	0	0	263	15/3
Butylacetyl ricinoleate	0	0	100	—	15/3
Butyl stearate	0	10	150	—	15/3
Rezyl X-315	0	0	10	200	15/3
Hydrogenated methyl abietate	0	0	100	—	15/4
Dicresyl Carbitol	0	0	25	150	15/2

simply, it appears that, in ratios below the maximum, the film exists as a solution of plasticizer in rubber chloride, and in ratios greater than the maximum, the film consists of a solution of rubber chloride in the plasticizer. Another concept would be to visualize compound formation between the chlorinated rubber and the plasticizer to the maximum, and from there on, solution of the compound in the plasticizer[8]. But certainly the effect noted is more important than the cause.

It appears that, until the plasticizer ratio exceeds its maximum, there is little actual plasticizing of the film which would be manifest in improved flexibility and the imparting of distensibility. Strength and stretch properties were studied on a number of these films, and it was found that stretch was never imparted until this critical plasticizer ratio was exceeded (Table VII). Likewise, where the flexibility, adhesion, and strength properties were considered, it was apparent that the plasticizer exhibited little beneficial action until this critical ratio was exceeded. All these results suggest that, in compounding chlorinated rubber and plasticizers to produce useful paints and lacquers, there is a definite minimum amount of plasticizer which may be advantageously incorporated. This critical plasticizer ratio is indicated by the hardness-loading curve, and may be defined as the point at which the continuity of the curve changes; in some cases it is a maximum, in some cases a leveling out, and in some cases merely an inversion in the curvature.



CONCLUSIONS

1. No particular solvent may be classified as the best for use with chlorinated rubber. On the contrary, the solvent must be chosen with a view to its general properties and, where other ingredients are to be compounded with chlorinated rubber, the solvent strength as measured by the dilution ratio is of considerable importance.

2. The compatibility of blown castor oil with chlorinated rubber, some other blown oils, and some alkyds, depends on the strength of the solvent used. Strong solvents as measured by their dilution ratio enhance compatibility.

3. No particular plasticizer is best for use with chlorinated rubber. Different plasticizers impart totally different results at different loading percentages. The choice of plasticizers is dictated by the ultimate properties desired. More frequently than not, the use of two or more plasticizers will be necessary to obtain the optimum properties for any given application.

4. Consideration of the fundamental principles and trends presented in this paper will be helpful in the formulation of chlorinated rubber finishes for a wider variety of uses, and products of an improved nature will be the result.

ACKNOWLEDGMENT

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PHYSICAL PROPERTIES OF POLYSTYRENE AS INFLUENCED BY TEMPERATURE *

T. S. CARSWELL, R. F. HAYES, and H. K. NASON

MONSANTO CHEMICAL COMPANY, SPRINGFIELD, MASS.

The physical properties of plastics are markedly influenced by the ambient temperature, but comparatively few quantitative data on polystyrene have been published. The variation of flexural strength and deflection at break for compression-moulded polystyrene and for a number of other compression-moulded plastic materials at temperatures from −70° to +200° C was described by Nitsche and Salewski[12]. Jenckel and Lagally[5] determined the tensile strength of extruded polystyrene filaments at 30° to 60° C. The elongation at 20° to 90° C was reported for extruded and racked polystyrene foil by Müller[11].

Since the mechanical properties of plastic materials are profoundly influenced by the methods used in preparing the test specimens, data on such properties are meaningless unless the details of preparation also are known. This paper describes variations in some of the mechanical properties of injection-moulded polystyrene over the range from −75° to +100° C. This method was chosen because injection moulding is by far the most commonly used commercial process for the fabrication of polystyrene.

PREPARATION OF TEST-SPECIMENS AND METHODS OF TESTING

Test-specimens were prepared from three grades of polystyrene whose average molecular weights were, respectively, 60,000, 95,000, and 115,000. Molecular weights were calculated from the viscosities of 0.2 per cent solutions of the polymers in toluene by means of the Staudinger relation[18]:

$$\frac{\eta_{sp}}{c} = K_m M$$

where η_{sp} = specific viscosity of solution
c = concentration of solution, unit moles of polymer per liter
M = molecular weight
K_m = the constant 1.8×10^{-4}

The specimens were injection-moulded on a Reed-Prentice injection-moulding machine of 2-ounce capacity. The test-specimen for the tensile and flexural tests was of the dumb-bell type (Figure 1) with a 4-inch length of uniform $\frac{1}{4} \times \frac{1}{4}$ inch cross-section. These specimens were injection-moulded at a heater temperature of 440° F, a ram pressure of 1100-1250 pounds per square inch, and a total cycle of 50 seconds. The specimen for the impact and hardness tests was a 5-inch length of $\frac{1}{2} \times \frac{1}{2}$ inch cross-section. Injection-moulding conditions were: heater temperature 450° F; ram pressure, 1200 pounds per square inch; total cycle, 60 seconds. All specimens were allowed to stand at least 72 hours at 25° C and 50 ± 2 per cent relative humidity before starting tests.

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Tensile and flexural data were obtained on a screw-type of tester, with a constant rate of cross-head movement. An insulated box (Figure 2) was constructed to house the grips for the tensile test and the supports for the flexural test. The testing temperature, which was varied from $-25°$ to $+100°$ C, was obtained by circulating through the insulated box dry air that had been heated by contact with a hot tube or cooled by contact with solid carbon dioxide. A temperature control accurate to within $\pm 1.0°$ for the range 0° to 90° C and to within $\pm 2.0°$ at $-25°$ and at $+100°$ C was obtained by this method. No attempt was made to control humidity, since the moisture absorption of polystyrene is negligible. Both tensile and flexural data were obtained with a constant rate of jaw separation of 1 inch per minute. The distance between supports in the flexural test was 2 inches.

The $\frac{1}{2} \times \frac{1}{2}$ inch bars for the impact test were conditioned for several hours at the desired temperature, and then tested immediately after removal from the conditioning atmosphere. Both Izod and Charpy test methods were used.[1]

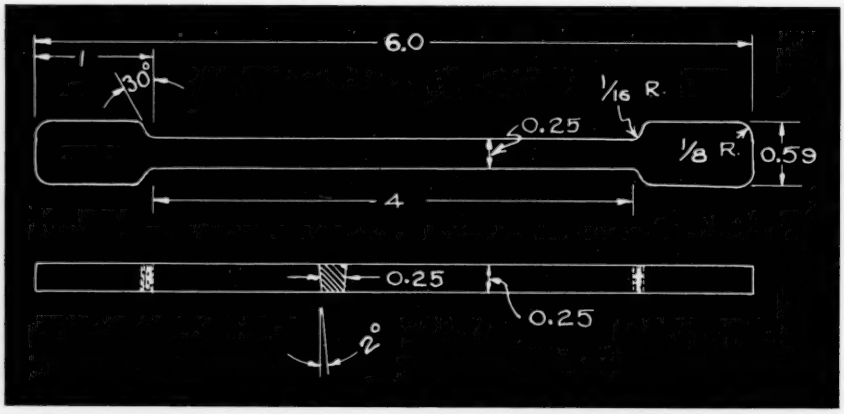

FIG. 1.—Monsanto tensile test specimen. (Dimensions in inches.)

The $\frac{1}{2} \times \frac{1}{2}$ inch bars remaining from the impact test were used for the indentation hardness test. These specimens were conditioned for several hours at the desired temperature, and were then tested as rapidly as possible after removal from the conditioning chamber. The Rockwell apparatus[2] was used, and all determinations were made on the M scale ($\frac{1}{4}$-inch ball, 100-kg. major load).

TENSILE AND FLEXURAL PROPERTIES

Tensile and flexural data at various temperatures from $-25°$ to $+100°$ C are presented in Table I and plotted in Figure 3. Both tensile strength and elongation increase with increase in average molecular weight of the polymer. The relation between flexural properties and molecular weight is not so clearly defined by these tests.

A critical transformation occurs at 80° to 85° C for all of the materials tested. At this temperature polystyrene changes from a hard, glasslike solid to a soft plastic. This transformation temperature coincides with the inflection point in the density-temperature curves for polystyrene reported by Patnode and Scheiber[13] and by Ueberreiter *et al.*[6, 7, 17]. It also corresponds to the inflection

point (or range) in the elongation and relaxation time curves of polystyrene reported by Müller[11], and to Russell's brittle point[16].

In this respect, polystyrene has a behavior similar to that of rubber, whose volume-temperature curve[3] exhibits a second-order transition range at −71° to −67° C. In rubber, too, this range is characterized by marked changes in mechanical properties and in heat capacity[3, 4, 8, 9, 14, 15, 19, 22]. Ueberreiter and his coworkers[6, 7, 17] pointed out this similarity in the shape of volume-temperature curves.

At temperatures above its transition range, polystyrene displays elastic properties and thermal retraction, as pointed out by Whitby[20, 21], and by Meyer,

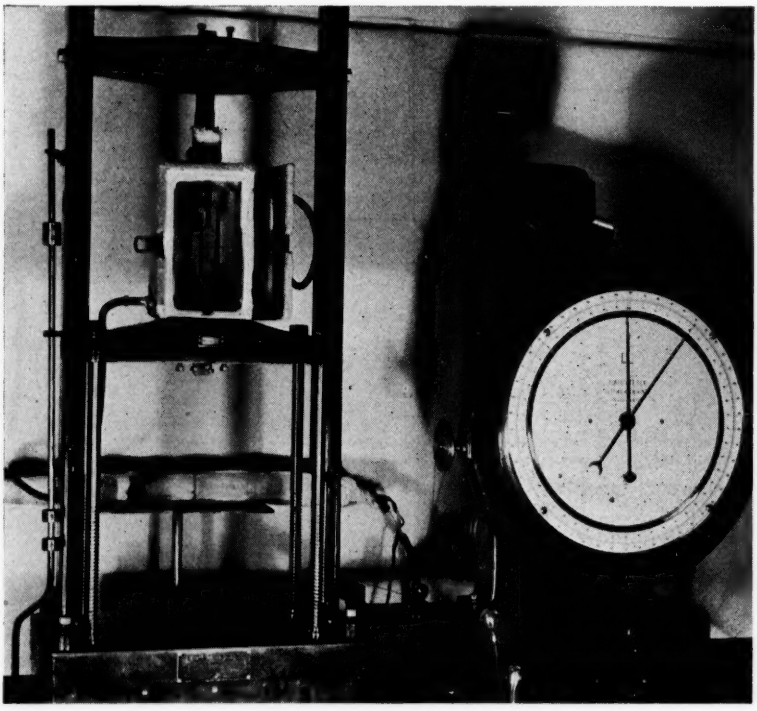

FIG. 2.—Apparatus arranged for tensile tests.

Susich and Valkó[10], and in these respects also the similarity to rubber is striking. In fact, polystyrene may be considered to be a rubberlike polymer whose critical transformation range occurs at a somewhat higher temperature than that of natural rubber.

As the ambient temperature is reduced below 80° to 85° C, the tensile and flexural strengths of polystyrene increase. This is the general tendency of plastic materials. However, the elongation and deflection at break of injection-moulded polystyrene also increase as the temperature is reduced, and this trend continues down to at least −25° C. This effect is unusual in a thermoplastic, as most such materials show reduced elongation and reduced ultimate deflection as the temperature is lowered. [Jenckel and Lagally[5] and Müller[11] reported elongation to decrease as the temperature was reduced. However, these workers studied ex-

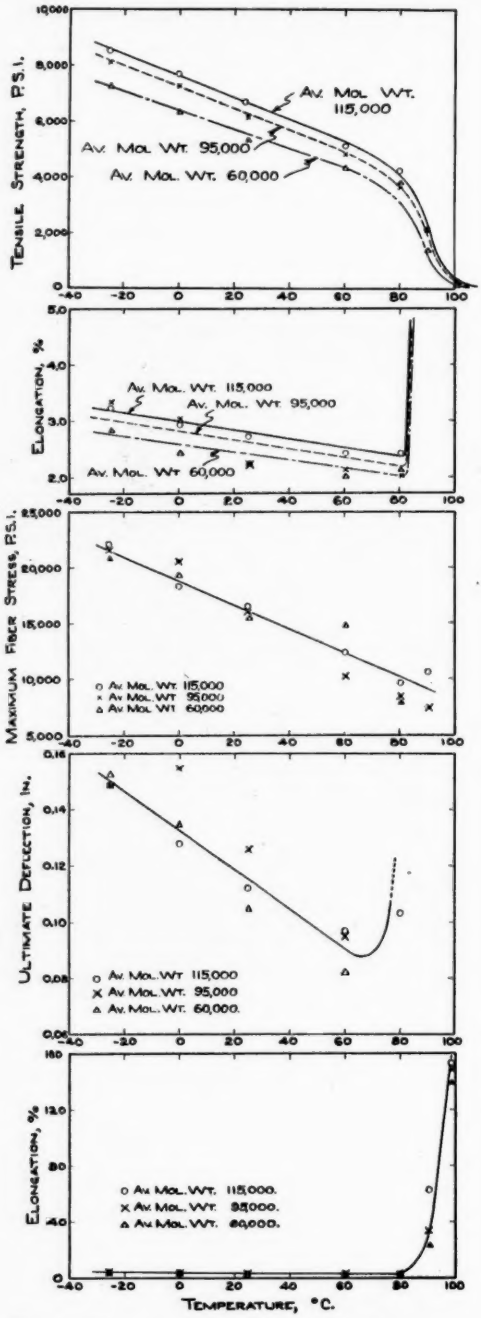
TENSILE STRENGTH, P.S.I.
Av. Mol. Wt. 115,000
Av. Mol. Wt. 95,000
Av. Mol. Wt. 60,000
ELONGATION, %
Av. Mol. Wt. 115,000
Av. Mol. Wt. 95,000
Av. Mol. Wt. 60,000
MAXIMUM FIBER STRESS, P.S.I.
o Av. Mol. Wt. 115,000
x Av. Mol. Wt. 95,000
Δ Av. Mol. Wt. 60,000
ULTIMATE DEFLECTION, IN.
o Av. Mol. Wt. 115,000
x Av. Mol. Wt. 95,000
Δ Av. Mol. Wt. 60,000.
ELONGATION, %
o Av. Mol. Wt. 115,000.
x Av. Mol. Wt. 95,000.
Δ Av. Mol. Wt. 60,000.
TEMPERATURE, °C.

FIG. 3.—Elongation of injection-moulded polystyrene.

truded filaments or foils, both of which were highly oriented by racking, and this may be expected to influence properties.]

These observations indicate that injection-moulded polystyrene does not become more brittle as the temperature is reduced but, on the contrary, actually becomes tougher under these conditions. In this respect it differs from most other plastic materials, especially from plasticized cellulose esters or ethers, most of which show greatly decreased toughness *i.e.*, increased brittleness, at the lower temperatures.

TABLE I

TENSILE AND FLEXURAL DATA ON POLYSTYRENE [a]

Temp. of testing, (° C)	Av. mol. weight	Ultimate tensile strength (lb. per sq. in.)	Ultimate elongation %	Ultimate flexural strength (lb. per sq. in.)	Ultimate deflection (inches)
25	60,000	7220	2.8	20,900	0.153
	95,000	8130	3.3	21,600	0.149
	115,000	8540	3.2	22,200	0.149
0	60,000	6300	2.4	19,350	0.135
	95,000	7230	3.0	20,500	0.155
	115,000	7700	2.9	18,400	0.128
25	60,000	5330	2.2	15,550	0.105
	95,000	6190	2.2	16,000	0.126
	115,000	6550	2.7	16,500	0.112
60	60,000	4350	2.0	14,800	0.082
	95,000	4860	2.1	10,100	0.095
	115,000	5030	2.4	12,450	0.097
80	60,000	3840	2.1	8,000	0.088
	95,000	3650	2.0	8,160	0.076
	115,000	4260	2.4	9,560	0.103
85	60,000	—	—	—	No break [b]
	95,000	—	—	7,400	No break [b]
	115,000	—	—	10,550	0.090
90	60,000	1510	33	—	—
	95,000	1710	63	—	—
	115,000	2240	28	—	—
100	60,000	305	147	—	—
	95,000	199	140	—	—
	115,000	302	152	—	—

[a] The average values for mean deviation of test results were: tensile strength, ± 200 lb. per sq. in.; elongation, ± 0.1%; flexural strength, ± 700 lb. per sq. in.; deflection, ± 0.0007 inch.
[b] Within deflection capacity of testing machine.

IMPACT STRENGTH

Impact strength data were obtained at a series of temperatures from −75° to +70° C. These data (Table II) confirm in general the results of the tensile and flexural tests, and show that there is at least no decrease in the toughness of injection-moulded polystyrene as the temperature is reduced below the transformation range, and that this trend continues down to at least −75° C. The results for the unnotched Izod test are shown graphically in Figure 4. (In general, the unnotched Izod method has been found the most satisfactory for testing the impact strength of polystyrene.)

The general increase in toughness with increase in average molecular weight of the polymer, which is indicated by the tensile test results, is confirmed by these impact data.

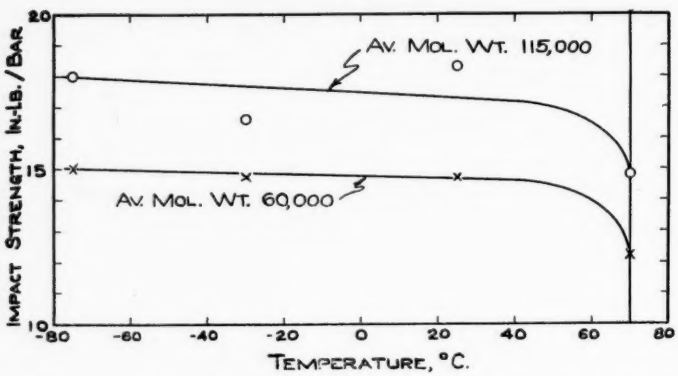

FIG. 4.—Izod (unnotched) impact strength of injection-moulded polystyrene per ½ x ½ inch bars.

INDENTATION HARDNESS

Hardness data, on the Rockwell M scale, are shown in Table III and Figure 5. Here again, a rapid change in values at or near the transformation temperature is noted. Also, indentation hardness is practically independent of molecular weight at temperatures below the transformation range.

TABLE II

IMPACT DATA

Test method	Av. mol. weight	Impact strength, in.-lb. per 0.5 x 0.5 in. bar			
		−75° C	−30° C	25° C	70° C
Charpy, unnotched ..	60,000	24.2 ± 1.5	23.8 ± 1.8	21.7 ± 2.1	17.6 ± 0.8
	115,000	25.7 ± 1.2	26.3 ± 4.2	26.2 ± 2.0	24.5 ± 2.4
Izod, unnotched	60,000	15.0 ± 1.4	14.7 ± 0.7	14.7 ± 0.6	12.2 ± 0.9
	115,000	18.0 ± 1.5	16.6 ± 1.1	18.3 ± 1.3	14.6 ± 1.8
Charpy, notched	60,000	1.82 ± 0.03	1.80 ± 0.03	1.89 ± 0.04	1.80 ± 0.05
	115,000	1.80 ± 0.03	1.77 ± 0.03	[a]	[a]
Izod, notched	60,000	2.2 ± 0.3	1.7 ± 0.5	2.3 ± 0.1	1.9 ± 0.4
	115,000	1.8 ± 0.5	2.1 ± 0.3	1.7 ± 0.3	1.9 ± 0.25

[a] Clean, straight breaks were not obtained, and the values were very irregular.

TABLE III

INDENTATION HARDNESS DATA

Conditioning Temp. (° C)	Hardness at av. mol. wt. of:	
	60,000	115,000
−70	124	124
−25	102	102
5	94	92
25	82	82
50	64	63
70	48	40
80	29	31
90	−70	−20

The exact determination of hardness was complicated by the impracticability of exposing the testing apparatus to temperatures far above or far below room temperature, and by the rapid change in surface temperatures of cooled or heated

specimens in contact with the highly conductive metal parts of the apparatus. The values shown in Table III for temperatures of 5° and 25° C are quite precise, as both specimens and testing machine were at the indicated temperature when the determinations were made. The other values given are approximate, and were obtained by conditioning the test-specimens to thermal equilibrium at the desired temperature and then testing as rapidly as possible on the Rockwell apparatus, which was at a temperature of 25° C. Hence, the hardness values given for −70° and −25° C are probably slightly lower than the true values for these temperatures, and the values for 50°, 70°, 80°, and 90° C are probably slightly high.

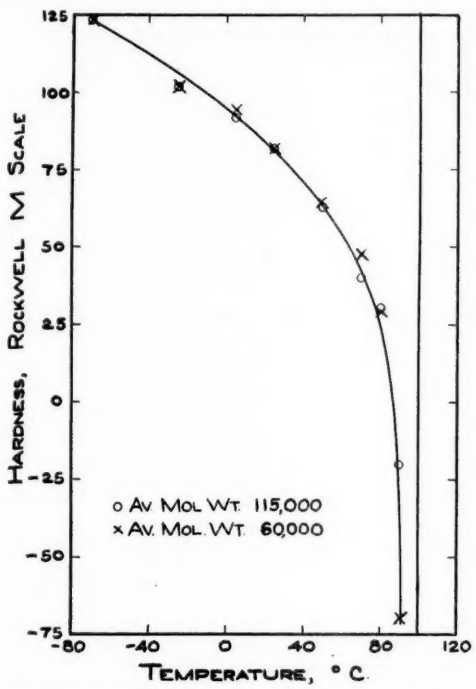

FIG. 5.—Indentation Hardness of injection-moulded polystyrene.

PRACTICAL IMPORTANCE

This increase in toughness at low temperatures, combined with other favorable physical properties, *e.g.*, negligible water absorption, good dimensional stability, freedom from taste and odor, wide range of color, and excellent mouldability, has been an important factor in the growing application of polystyrene in industrial fields where physical and mechanical stability are important. Panels, drip trays, doors, etc., in recent models of mechanical refrigerators are good examples of such applications.

ACKNOWLEDGMENT

We are deeply indebted to W. E. Tucker, Jr., who conducted most of the laboratory tests.

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THE EFFECT OF TEMPERATURE ON THE SUNLIGHT DETERIORATION OF A RUBBER COMPOUND *

J. M. Ball and C. E. Bradley, Jr.

R. T. Vanderbilt Laboratory, East Norwalk, Connecticut

The subject of this article might be the question: "Does temperature have an effect on the deterioration of rubber in sunlight and, if so, approximately how much effect?" We are interested in any effect of temperature because rubber goods in service are frequently subjected to sunlight over a fairly wide temperature range. There are apparently very few references or comments in the literature on this subject; but we wish to look briefly at some significant experiments of the past which have to do with sunlight without regard for temperature, and then discuss a new experiment.

EXPERIMENTS OF THE PAST

In 1885 William Thomson, the famous British scientist, in an address before the Society of Chemical Industry, entitled "India Rubber and its Decay"[1], described an experiment in which he stretched rubber threads and sealed them in tubes containing air, oxygen, carbon dioxide and hydrogen, respectively. Another set of tubes was evacuated. All tubes were exposed to direct sunlight each day for several months. After a few days' exposure, the threads in oxygen broke, and at the end of the exposure period, the threads in air were rotten. The threads in the other tubes were sound at the end of the period.

In 1903 C. O. Weber published a paper entitled "On the Action of Light on India Rubber"[2]. In his experiments, cured and uncured Para, worked and overworked, were exposed to sunlight for fifty days. The acetone extract increased during this exposure period to an extent which depended on the degree of overworking and also on the percentage of combined sulfur.

In 1926 Williams published a paper entitled "Oxidation of Rubber Exposed to Light"[3], in which he stated that the oxidation of rubber is speeded greatly by the presence of ordinary light, especially when the rubber is in a strained condition. He placed buffings from a pure-gum inner tube in two glass bulbs containing oxygen, one covered with tin foil, the other exposed to July sunlight. In the exposed tube, the rate of oxygen absorption was seven times greater than in the unexposed tube. Williams also put strips of a gray sidewall stock, stretched five per cent, in sealed glass tubes, one containing air, one containing oxygen, and one evacuated. These tubes were exposed to July sunlight continuously each day for two weeks. The surface of the strips in air and in oxygen became slightly wrinkled, whereas the strip in the evacuated tube appeared to be unchanged.

In 1930 J. C. Howard and H. C. Boehmer, of the Kaufman Rubber Co., Kitchener, Ontario, bent samples of ordinary black footwear-upper, approximately

* Reprinted from *The Rubber Age* (New York), Vol. 50, No. 6, pages 425-430, March 1942. It is based on a paper presented before the Ontario Rubber Section of the Canadian Chemical Association, October 16, 1941.

$\frac{1}{16}$-inch thick, around a mandrel $\frac{3}{8}$-inch in diameter, and placed them inside a clear quartz tube about 6 inches long and $1\frac{1}{4}$ inches in diameter. Samples were exposed during the summer under the following conditions: (1) tube open and filled with air at atmospheric pressure; (2) tube closed and filled with hydrogen at atmospheric pressure; (3) tube evacuated. The usual atmospheric cracking occurred in the tube containing air, whereas no cracking was observed under the other two conditions. It was concluded that the cracking was caused by ozone formed by the action of sunlight on oxygen at the surface of the rubber.

THE PRESENT EXPERIMENT

We learn from these experiments that there must be some connection between oxygen and sunlight deterioration. The experiments were not, of course, intended to study the possible effect of temperature on such deterioration. Nevertheless, it was felt that the effect of temperature might be interesting and, accordingly, the Vanderbilt Laboratory undertook this work. The study was made at four temperatures, *viz.*, −30° C, +20° C, 70° C and 100° C, with two different periods of exposure, *viz.*, 4 and 7 hours.

It was desired to use a good tire-tread compound, but such a compound does not deteriorate fast enough in sunlight to be suitable for an experiment which is likely to involve a big bill for dry ice. Consequently, the following compound was used, the cure being just about sufficient to avoid bloom:

Test Compound

Smoked sheet	100
Zinc oxide	5
Gilder's whiting	60
Sulfur	4
Diphenylguanidine	1.25
	170.25

Laboratory press cure:—20 minutes at 307°F

APPARATUS

Dumb-bell test-specimens about 0.020 inch thick, both unstretched and stretched 10 per cent, were exposed to sunlight under Vitaglass in wooden boxes about 10 inches square, coated on the outside with aluminum paint and insulated on the inside with Celotex. The bottom of the boxes contained the heating or cooling coils, and the samples were stretched or rested on a wooden frame placed near the top of the box. Three thermometers were used in each box, one placed under the samples and two over the samples. One of those placed over the samples was first dipped several times in a self-curing cement of the stock until a total thickness of stock corresponding to the thickness of the dumb-bells was obtained around the bulb. The thermometer bulb covered with that stock was then placed in an oven at 70° C for 1 hour, at the end of which time thorough vulcanization had occurred. The lowest two temperatures, *viz.*, −30° C and +20° C, were obtained with cooling coils; and the highest two temperatures, *viz.*, 70° C and 100° C, were obtained with heating coils.

A small, wooden propeller revolved continuously in each box on a vertical shaft extending through the bottom of the box. The cooling coils contained circulating acetone, supplied from a separate tank enclosing larger coils imbedded in dry ice. A storm window, enclosed on both top and bottom by Vitaglass and Corex-D glass, respectively, was screwed to the top of each box, thus pro-

viding a cover as well as an insulating air space about one inch thick to prevent frosting, which would otherwise have occurred on the coldest box. Thus, sunlight had to pass through two layers of glass, each about $\frac{1}{16}$-inch thick. Also, on the top of the coldest box, 40-gauge Nichrome heating wires about $\frac{1}{2}$-inch apart were placed in contact with the Vitaglass, and were kept hot to make doubly sure there would be no frosting. Both the boxes and the storm windows contained wire-gauze tubes of calcium chloride sufficient to prevent condensation. Furthermore, through each storm window a single glass-tube containing cold circulating acetone was inserted to condense on it the last objectionable trace of moisture. Figure 1 is a photograph of the $-30°$ C box, showing the cooling coil, the propeller, the samples, thermometers and storm window.

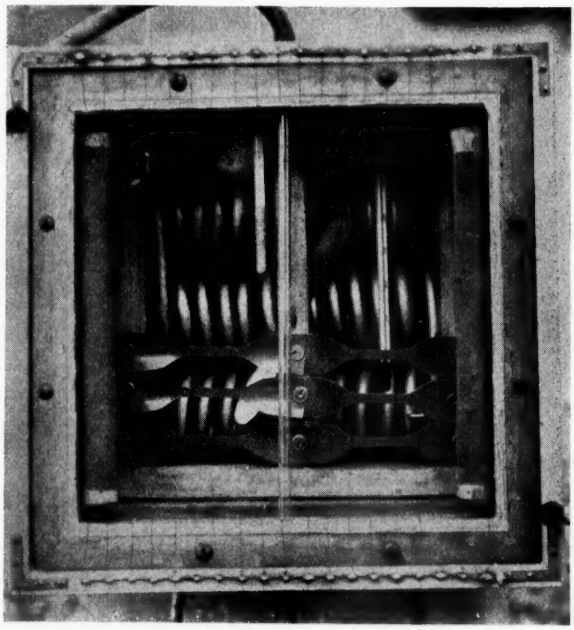

FIG. 1.

The boxes were mounted on a large wooden rack kept approximately perpendicular to the sun's rays throughout the exposure period. Duplicate sets of stretched and unstretched dumb-bells were mounted on uncovered boards placed on the rack beside the boxes. Figure 2 is a photograph of all the boxes and uncovered samples as assembled on the roof of the Vanderbilt Laboratory at East Norwalk, Connecticut.

Figure 3 illustrates the transparency of Vitaglass to solar ultraviolet radiation. This glass transmits a large proportion of the ultraviolet, *i.e.*, about 20 per cent at 2,900 a.u. and about 85 per cent at 4,000 a.u. It was desired to use Corex-D glass, which is understood to be even more transparent to ultraviolet radiation, but a sufficient amount could not be obtained in time. Ordinary window-glass cuts off a much larger part of the ultraviolet radiation of sunlight than does Vitaglass. The sole aim was to let as much sunlight as possible through to the rubber.

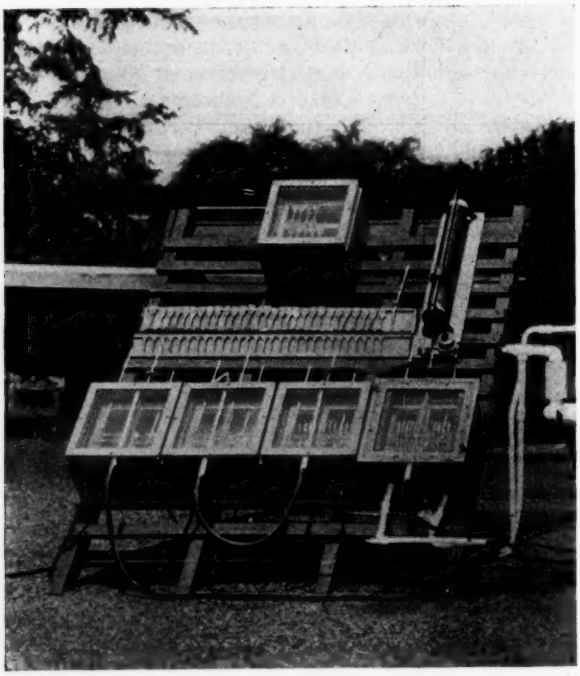

FIG. 2.

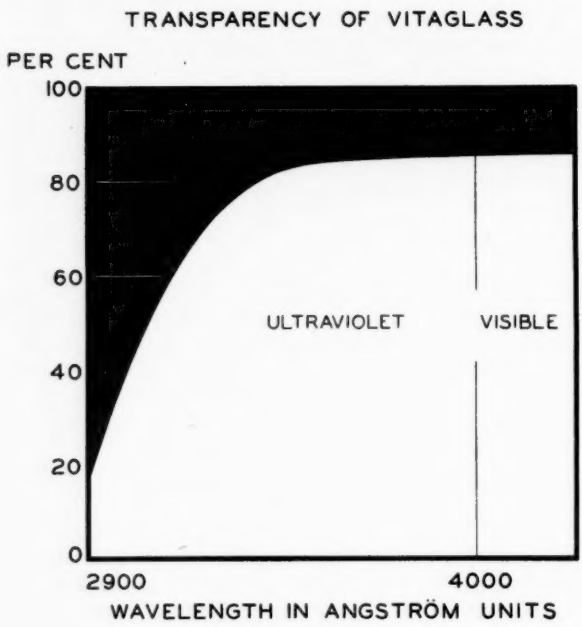
TRANSPARENCY OF VITAGLASS
PER CENT
100
80
60
40
20
0
ULTRAVIOLET
VISIBLE
2900
4000
WAVELENGTH IN ANGSTRÖM UNITS

FIG. 3.

TABLE OF TENSILE PROPERTIES

Stress at 300% (S)—Tensile (T)—% Elongation (E)

	First Period 4 Hours			Second Period 7 Hours		
	Darkness Controls					
	S	T	E	S	T	E
−30°C. Unstretched	585	2630	560	585	2650	560
−30°C. Stretched	585	2600	555	585	2640	555
+20°C. Unstretched *	590	2650	560	590	2650	560
+20°C. Stretched	585	2580	555	590	2500	560
+45°C. Unstretched	590	2700	555	610	2780	550
+45°C. Stretched	585	2650	555	605	2770	555
+70°C. Unstretched	675	2810	550	700	2730	550
+70°C. Stretched	675	2780	560	640	2560	540
+100°C. Unstretched	745	2060	500	730	1870	475
+100°C. Stretched	680	1965	500	695	1860	480
			Exposed Samples			
−30°C. Unstretched	670	2220	520	690	2200	530
−30°C. Stretched	650	2140	520	660	2220	530
+20°C. Unstretched	640	1740	490	685	1345	445
+20°C. Stretched	650	1680	485	680	1310	465
+45°C. Unstretched †	645	1500	470	655	1255	420
+45°C. Stretched †	650	1600	475	660	1190	425
+70°C. Unstretched	600	1120	440	—	420	180
+70°C. Stretched	590	925	430	—	420	200
+100°C. Unstretched	620	845	390	—	390	204
+100°C. Stretched	540	830	420	—	390	240

* This control has the same properties as the original, unexposed control.
† Uncovered.
Note: Free sulfur apparently tended to decrease, and acetone extract to increase during exposure, but the time of exposure was not long enough to justify any definite statement regarding these determinations.

TEMPERATURE MEASUREMENTS

The three thermometers in each box agreed among themselves within 5° C, with the exception of the room temperature box, which showed somewhat wider variation. The three thermometers for the uncovered samples recorded about 45° C, and agreed among themselves within about 8° C. The two periods of exposure, 4 and 7 hours, were made on August 6, 1941, from about 9 A. M. to 4 P. M., Eastern Daylight Saving Time. There was continuous brilliant sunshine that day. A supply of control slabs was kept in a dark closet; and additional control samples were obtained by heating in an oven at 45°, 70°, and 100° C for 4 and 7 hours, and by cooling in the dark to −30° C for the same two periods.

RESULTS

Let us see now what happened to the tensile strength of all the samples, stretched and unstretched, covered and uncovered, exposed and unexposed, at the various temperatures. Let us begin with the lowest temperature, *i.e.*, −30° C.

The accompanying graphs show tensile strengths plotted against hours of aging. The tensile strength of the unstretched samples are represented by a solid line, and the tensile strengths of the stretched samples by a broken line. The two lines representing the exposed samples are marked SUNLIGHT, and the two lines representing the control samples are marked DARKNESS.

Figure 4 is the graph for −30° C, and it is evident that sunlight does have an effect, even at this low temperature, as the tensile strength of the exposed samples drops in 7 hours from about 2,650 to about 2,200 pounds per square inch. The stretched samples show about the same tensile strengths as the unstretched.

Figure 5 is the graph for +20° C. The deterioration due to sunlight is greater than at −30° C, but otherwise this graph is much the same as the previous one.

Figure 6, the graph for 70° C, is quite different from the first two. The control

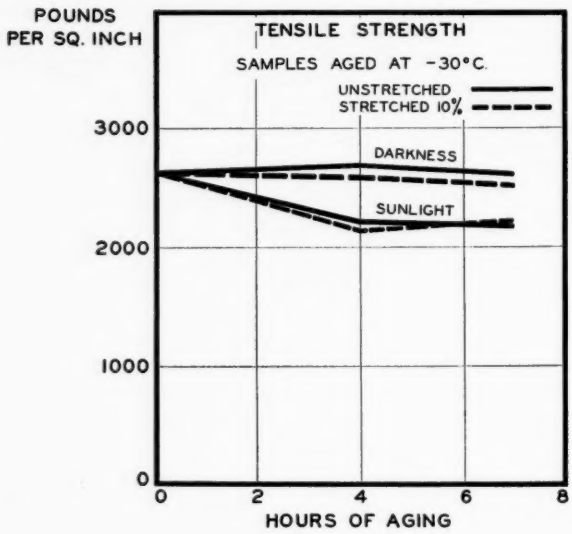

FIG. 4.

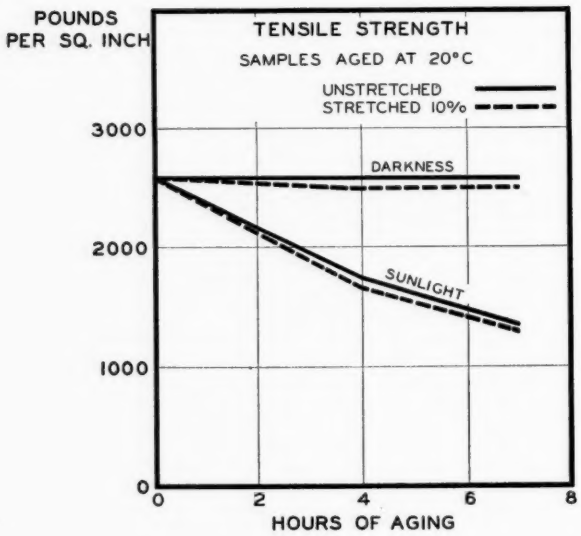

FIG. 5.

samples which were in darkness in the oven actually increased in tensile strength, as is characteristic of some stocks, whereas the samples in sunlight deteriorated badly. Here again, however, there is not much difference between the stretched and unstretched samples.

Lastly, Figure 7, shows the results at 100° C. For the first time the control samples, *i.e.*, those heated in the oven, deteriorated in tensile strength. The

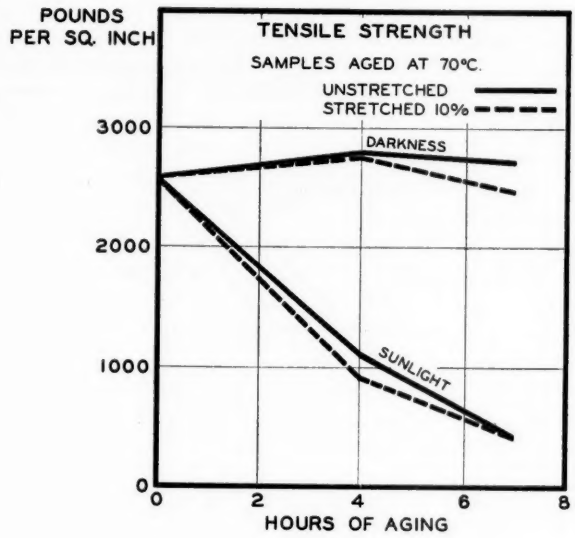

FIG. 6.

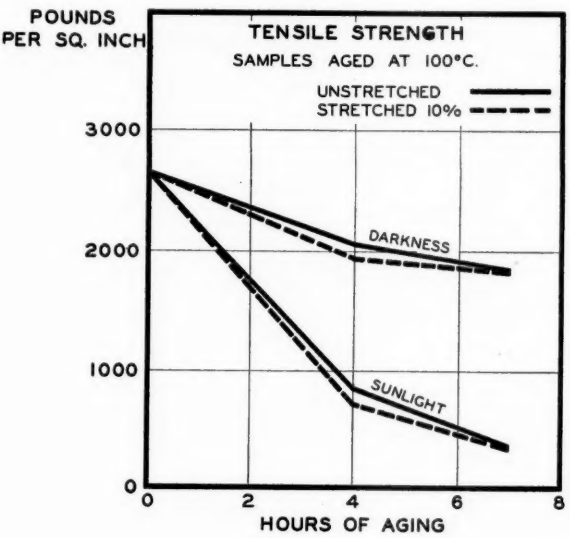

FIG. 7.

exposed samples lost more strength than those at 70° C, but the spread between the control and the exposed samples is a little less at 100° C than at 70° C. The deterioration in sunlight is about three times as great as that in the oven.

APPEARANCE OF THE SAMPLES

Exposure to sunlight resulted in the formation of a surface skin on the exposed side of both stretched and unstretched samples at each temperature except at −30° C, but atmospheric cracking did not occur at any temperature. The surface skin was noticeable particularly because it cracked while the dumbbells were being tested on the Scott machine. The underside of the samples did not show surface skinning, and in darkness there was no surface skinning at any temperature. Longer periods of exposure in sunlight would undoubtedly have caused atmospheric cracking on the underside.

SUMMARY OF TENSILE RESULTS

Having shown the results at the four temperatures on separate graphs (Figures 4, 5, 6, and 7), it seemed desirable to show all the temperatures together on

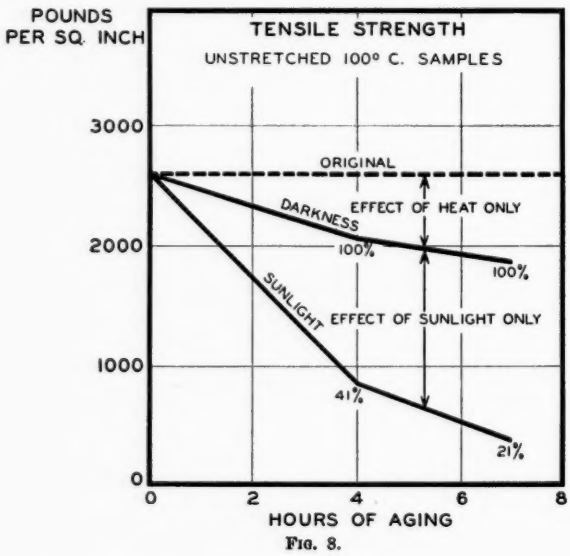

FIG. 8.

one graph. Since there was very little difference between stretched and unstretched samples, attention was confined to unstretched samples in constructing this composite graph.

Figure 8 shows again the results for 100° C, plotted in a slightly different way. The space between the horizontal line for original tensile strength and the DARKNESS line represents the effect of heat alone, and the space between the DARKNESS line and the SUNLIGHT line represents the effect of sunlight alone. The 4-hour and 7-hour tensile strengths for the darkness controls are both marked on this graph as 100 per cent, and those for the exposed samples are marked 41 per cent and 21 per cent, respectively, meaning that these are percentages of the control tensile strengths.

Figure 9 is a variation of the previous graph, showing the effects of sunlight alone, and plotting percentages of the control tensile strengths instead of actual tensile strengths. In other words, the control samples are represented by a hori-

zontal line taken as 100 per cent throughout, and the SUNLIGHT samples are represented as percentages of that horizontal control line.

This leads to Figure 10, which contains all the various temperature lines. Included also are the results for the uncovered samples, which are shown as a broken line. This broken line lies between the 20° C and 70° C lines. This graph, then, indicates that temperature has a strong effect on the sunlight deterioration of the compound studied. The graph represents the net effect of sunlight after

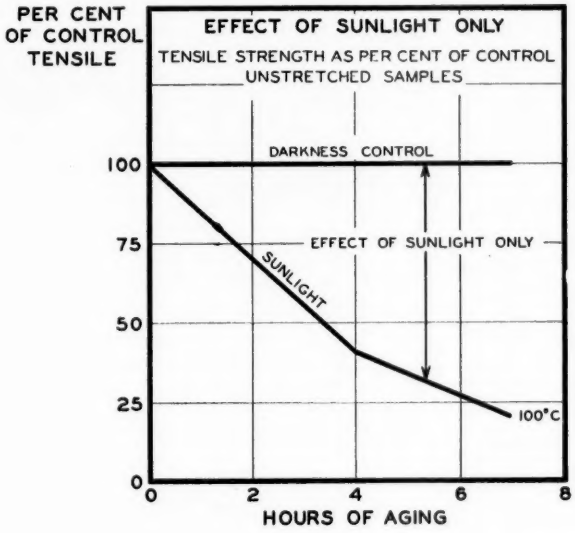

FIG. 9.

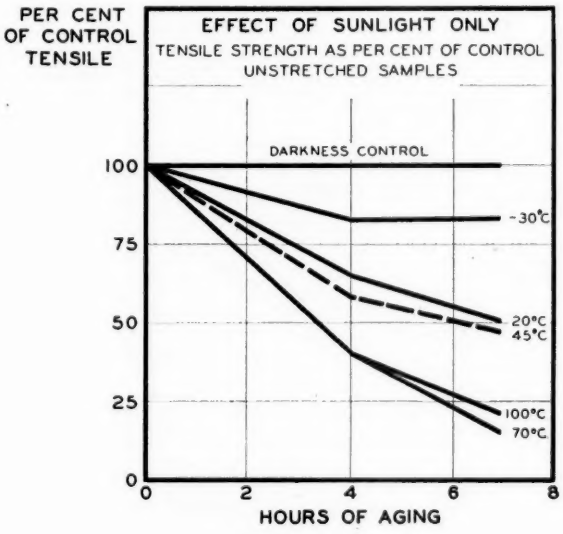

FIG. 10.

the purely heat effect or change in darkness has been subtracted from the total or overall change. How important is this temperature effect? The last graph proves that, at 20° C, the effect of sunlight alone is two or three times that at −30° C and that, at 70° C, the effect is about 1.75 times that at 20° C.

ACKNOWLEDGMENT

In conclusion the authors wish to thank A. A. Somerville and E. B. Curtis for permission to use our laboratory, and W. H. Scott, Jr., who helped design and build the apparatus, and who drew the graphs.

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FURTHER ELECTRON MICROSCOPE STUDIES ON COLLOIDAL CARBON, AND THE ROLE OF SURFACE IN RUBBER REENFORCEMENT *

W. B. WIEGAND

COLUMBIAN CARBON CO., NEW YORK, N. Y.

PARTICLE SIZE AND SURFACE

Using the method of a previous publication[1], the following results for colloidal carbons which have been used in rubber were obtained. The values assigned are tentative, and accuracy better than 20 per cent is expressly disclaimed. The magnification (final) was 50,000 in all cases.

Carbon	Mean diameter ($m\mu$)	Surface (acres per lb.)
Coarse thermal (Thermax)	274	1.1
Lampblack (Rubber Velvet)	97	2.6
Semireënforcing (Furnex-Gastex)	81.5	3.7
Fine thermal (P-33)	74	4.1
Acetylene (Shawinigan)	43	7.3
Statex (Columbian)	34	8.4
Carbon black (Micronex)	28	10.6
Color carbon (Super-Spectra)	13	22.2

PARTICLE SHAPE AND DISTRIBUTION

Spherical shape preponderates in all cases. Considerable variations in distributions with tendency toward right-handed skewness. Acetylene black and lampblack pictures show irregular networks of contracting particles; other carbons are particulate and flocculate.

The absence of elongated or acicular habit in semireënforcing carbons, lampblack, and acetylene carbon necessitates a new theoretical approach to the problem of modulus and hardness. The rubber-compounding properties of the carbons are therefore reviewed in some detail over the loading range from 20 to 150 per cent by weight on the rubber.

RUBBER COMPOUNDING STUDIES

Energy.—Micronex, Statex, and semireënforcing carbons reach maximum at about 50 per cent; P-33 at higher loading; acetylene and lampblack at much lower loadings.

Tensile strength.—The same general distinction holds. Acetylene in both cases is more extreme than lampblack.

Modulus (*L*-300).—Sharp reversals from energy and tensile with respect to order. Acetylene highest; lampblack second; Micronex, Statex, and semireënforcing blacks third (as a group); P-33 much the lowest.

* Reprinted from the *India Rubber World*, Vol. 105, No. 3, pages 270-272, December 1941. This paper is a condensed version of a paper presented before the Ontario Rubber Division of the Canadian Chemical Association, Kitchener, Ontario, November 14, 1941.

Shore hardness.—Similar to modulus, excepting lampblack and semireënforcing carbons, which are lower than carbon black, indicating that their stress-strain curves have crossed at the lower elongations.

Rebound resilience.—Carbon black much the lowest; Statex and acetylene black nearly equal; then semireënforcing carbons, lampblack, and P-33 in increasing order.

Raw plasticity.—Inverse order to Shore hardness. Carbons producing softest raw stocks produce softest cured stocks.

Electrical resistivity.—Influence of fineness and purity obscured by other factors. Acetylene black much the lowest. Statex next. Lampblack much lower than semireënforcing carbons although both coarser and less pure. Semireëforcing carbons overtake carbon black at approximately 90 per cent loading; lampblack at 55 per cent. Evidence that lampblack and acetylene black reach lower values than justified by either particle size or composition.

ADVANTAGES OF SOFT CARBONS

Details of development, manufacture, and application in natural and synthetic rubber. Figure 1 illustrates some general principles involved. Synthetic rubbers,

FIG. 1.—Advantages of semireënforcing carbons in natural and synthetic rubber.

being harder, less resilient and less extensible than natural rubber, are even more dependent than the natural product on soft carbons.

SURFACE CHEMISTRY AND BEHAVIOR IN RUBBER

Analysis of detailed tabular comparison shows that:

(1) pH and vulcanizing behavior can be related to carbon dioxide content in volatile substances.

(2) Neither total volatile substances nor their composition correlates with reënforcing properties and distinctions.

(3) Carbons of similar area may show almost identical chemical analysis, yet behave very differently in rubber.

These results turn attention back to the carbon itself and its behavior as a colloid.

COLLOIDAL PROPERTIES AND SURFACE AREA

Detailed tabular comparison with surface values from one acre to 22 acres reveals:

(1) Apparent density decreases with increasing surface, but acetylene black and lampblack are lower and thermal blacks higher than expected.

(2) Sedimentation volume in alcohol and benzene increases, but acetylene and lampblack are much higher than justified by their surface.

(3) Gloss of torn surface in a 50 per cent cured tread stock increases with surface, but lampblack and acetylene black are duller than expected.

(4) The bound rubber value for thermal carbon is lower than expected.

(5) When ground into a Glyptol enamel, acetylene black and lampblack show a much duller surface than that of other carbons whether smaller or larger in particle size.

These results suggest significant and persistent differences in interparticle and in particle to vehicle attachment.

COLOR, STRENGTH, AND OIL ABSORPTION *VS.* SURFACE AREA

Data are shown in Figure 2, from which it is noted that:

(1) Tinting strength rises sharply from one acre to eight acres, thereafter remaining comparatively constant up to 22 acres.

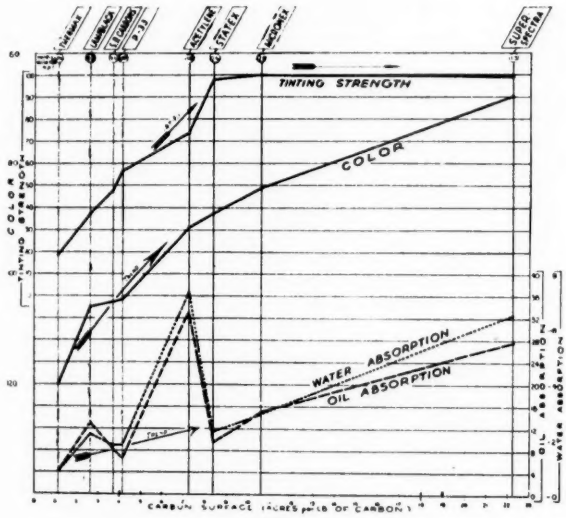


FIG. 2.

(2) Color (in mineral oil) rises continuously, although at diminishing rate to the limits of the present series (the good color of lampblack is attributable to its content of many very finely divided particles).

(3) Oil and water absorption values trend generally upward with increasing surface, but are subject to violent fluctuations.

The following anomalies appear:

(4) Acetylene carbon is very high in absorption and low in strength. Lampblack is also high in absorption (without sensible anomaly in strength).

(5) Thermal carbons are low in absorption, but normal in strength.

(6) Semireënforcing carbons, Statex, and carbon blacks are taken as normal, establishing the trends discussed under (1), (2), and (3) above.

The above, plus the colloidal properties previously discussed, suggested as a working hypothesis that:

(a) Acetylene black and lampblack assume, in liquid vehicles, an altered pigment structure or disposition, consisting of carbon-to-carbon complexes or networks, which increase the rigidity and therefore the absorption values, but which, when sufficiently marked, detract from strength (ability to darken a white paste of zinc oxide).

(b) These complexes do not detract from the effect of increasing surface on the absorption of light (normal "color").

(c) Thermal carbons show depressed absorption of vehicles plus entire absence of carbon-to-carbon structure (normal strength).

With this background, it is now possible to approach the role of surface in rubber reënforcement.

RUBBER PROPERTIES AND SURFACE AREA

(a) Oil, water, and rubber absorptions—plasticity, hardness and modulus—Figure 3.

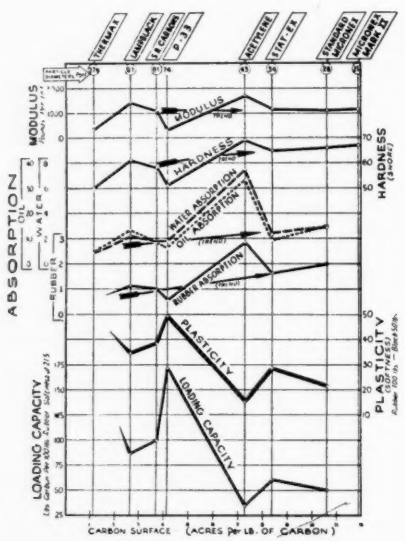


FIG. 3.

The oil and water absorption of Figure 2 are reproduced. Beneath them is the rubber absorption curve derived from, and the reciprocal of the plasticity values referred to, an arbitrary point of 21.5 on the Goodrich plastometer softness scale.

Above them are curves for Shore hardness and for L-300 modulus in a 50 per cent mercaptobenzothiazole-accelerated tread mix at best cure.

The trends and the anomalies are strikingly similar. Liquid absorption behavior of carbons ranging from one acre to 12 acres is carried over into raw and

even into cured rubber. The network structure or arrangement of the carbon particles survives the shearing forces of the rubber mixing mill (acetylene black and lampblack). Likewise, the inactivity of the thermal carbon particles whether toward the rubber phase or toward each other. Semireënforcing carbons, Statex, and carbon black again constitute the norm.

Broadly, the consistency of raw or cured rubber, as of liquids, is dominated less by carbon surface than by carbon structure.

(b) Energy, tensile and rebound—Figure 4.

Shore hardness and L-300 modulus are repeated from Figure 3 as liaison.

Energy, like tinting strength (Figure 2) is dominated by surface from one acre to eight acres, thereafter flattening. Tensile strength continues a steady rise up to (and beyond) the 12-acre point (cf. Color). In both cases, however, acetylene carbon is far below its surface expectancy, lampblack less so.

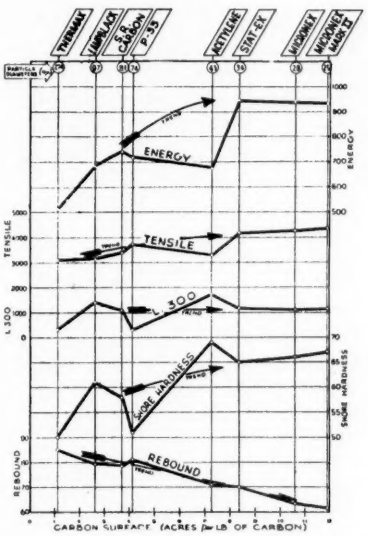


FIG. 4.—50 lbs. carbon per 100 lbs. rubber.

Modulus, as already intimated, is so affected by carbon structures (+) and by inertness (−) as to present little discernible response to increasing surface. In Shore hardness, otherwise of similar trend to L-300 modulus, surface reasserts its upward influence.

Rebound resilience alone responds consistently to carbon surface. Apart from faint residues of lampblack and acetylene deficiency and at P-33 extra resiliency, the curve is a straight line function of surface, and its extrapolation to the Super Spectra value (22 acres) squares with the facts within experimental errors.

It is noted in this connection that the extent of deformation involved in Healey pendulum testing (approximately 20 per cent) is lower than in Shore-hardness (approximately 50 per cent) and is, in fact, the lowest point on the stress-strain curve which is evaluated in customary rubber testing.

The influence of internal carbon-to-carbon structure on reënforcement appears to be sensitive to the degree of distortion involved. This suggests that a minute study of the whole stress-strain curve (particularly in its lower reaches) may throw light on the type of structure present.

TABLE I

CLASSIFICATION OF RUBBER CARBONS

Type	Carbons	Action in rubber	Rubber compounding properties	Tinctorial properties	Colloidal properties
I	Carbon black Statex Semireënforcing carbon	Form reënforcing "carbon-rubber" complexes	Normal reënforcement, extent of which governed by specific surface of carbon	Normal trend Strength rising to maximum Color rising continuously Reënforce "active" vehicles in proportion to specific surface	Density, sedimentation-volumes, oil and water absorption and bound rubber essentially normal, *i.e.*, follow surface values
II	Acetylene black Lampblack	Form both carbon-rubber (C-R) and carbon-carbon (C-C) complexes	Energy and tensile low, due to C-C complexes interfering with C-R complexes Raw plasticity and loading capacity low Modulus and hardness high—due to additive effect of C-C and C-R complexes Electrical anisotropy and conductivity high	Strength low (acetylene) Color normal Always form matte or dull surfaces in inks and paints Surface of torn rubber duller than Types I and III	Density low Sedimentation volume high Liquid absorptions high, due to carbon-carbon network
III	Fine thermal Coarse thermal	Inactive—form no complexes	Primary action dilution, but tensile strength improved by fine thermal carbon via plastic film mechanism	Strength and color normal for particle size Inactive to all vehicles	Density high Sedimentation volume low Liquid absorptions low Bound rubber low carbon surface inactive

CONCLUSIONS

(1) Based on preliminary electron microscope analysis, rubber carbons are assigned tentative surface values, ranging from one to upward of 12 acres per pound.

(2) In all cases particles are of essentially spherical habit.

(3) Indications of chain and network structure have appeared in acetylene carbon and lampblack plates (conclusion not final).

(4) Physical properties of carbons in rubber are reviewed, and the advantages of "soft" carbons enumerated.

(5) Differences in chemical compositions are found not to square with reënforcing differences in rubber.

(6) When colloidal properties, tinctorial properties, and rubber properties are plotted against acres per pound, it is found, as anticipated, that surface is, in general, the dominating influence; subject, however, to important and sometimes controlling anomalies.

(7) These anomalies appear to be largely resolved on the assumption that three broad types of carbon behavior exist.

(I) Carbon-rubber complexes (reënforced rubber) are formed (examples—semireënforcing carbons, Statex and carbon blacks).

(II) Carbon-carbon complexes or networks are formed in addition to (I). Examples, acetylene carbon and lampblack.

(III) Carbons are inert—neither (I) nor (II) occurs. Examples—thermal carbons.

These relations are brought together in Table 1.

REFERENCE

[1] "The particle size and shape of colloidal carbon as revealed by the electron microscope", Columbian Carbon Co. Research Laboratories, RUBBER CHEM. TECH. **14**, 52 (1941).

COLLOIDAL CARBON AS REVEALED BY THE ELECTRON MICROSCOPE *

WILLIAM B. WIEGAND and WILLIAM A. LADD

COLUMBIAN CARBON CO., NEW YORK, N. Y.

The electron microscope of today may be said to rest on the pioneer work of three outstanding physicists. J. J. Thompson, in 1897, discovered electrons under the name of negative corpuscles. De Broglie, about 1922, established the wave characteristics of electrons. In 1926 Busch established the electron lens.

In 1935, E. F. Burton, following a visit to Germany, envisaged the enormous potentialities of the electron microscope and began a program at Toronto designed to eliminate the serious defects of early German instruments. In 1938, this program culminated in the construction of a new and superior instrument by two of his graduate students, A. Prebus and J. Hillier.

The publication of their results early in 1939 aroused the immediate interest of the Columbian Carbon Company which later established a Fellowship at Toronto under Professor Burton's direction. In 1940, A. Prebus, assisted by W. A. Ladd, working in Toronto, secured for Columbian the first perfect pictures of Micronex, from which accurate data as to mean surface area and as to particle shape were obtained. Public release followed in June, 1940.

Prebus is now Professor at Ohio State University and is pursuing the theoretical side. Hillier is at R. C. A., where instruments, of essentially Toronto design, are being developed commercially, and Ladd has joined the Columbian Carbon Research Laboratories, for the two-fold purpose of further improving the microscope and of applying it to the problems of natural and synthetic rubber reënforcement.

This work of Professor Burton and his pupils is of importance under present critical conditions since the replacement of natural by synthetic rubber necessitates a new approach to the theory and practice of rubber reënforcement. With the aid of the electron microscope, it is now for the first time possible to evaluate the role played by surface area in carbon-rubber reënforcement.

THE ELECTRON MICROSCOPE

The elements of the electron microscope are directly analogous to the light microscope; a source of illumination, condensing lens, objective and projective lenses. Fundamental differences are: electrons replace light, magnetic coils replace glass lenses. The electrons are accelerated by a potential difference supplied by an 85,000-volt d.c. rectifier. Magnifications are measured by removing the pole-piece in the projection lens, displacing the object by differential micrometer screws, and measuring the resulting displacement in successive photographs.

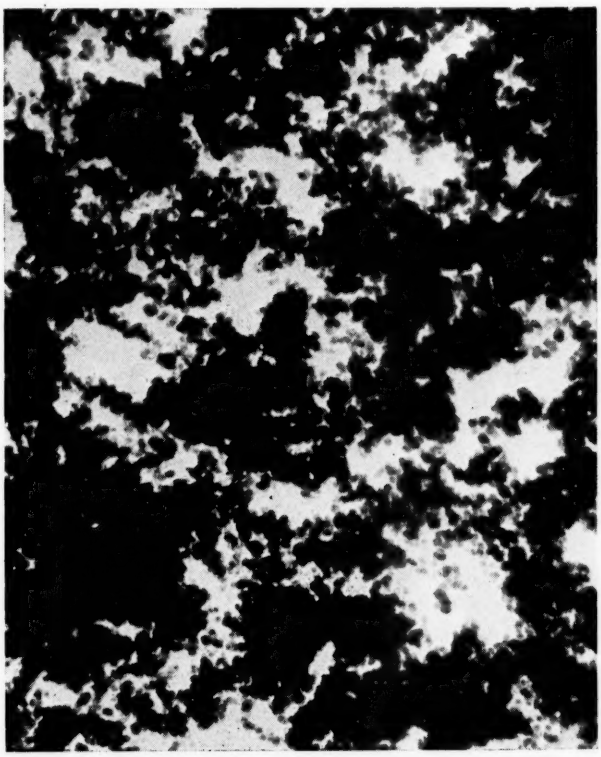
The object is supported by a collodion film 15-20 millimicrons thick. This film is in turn supported by a 200-mesh screen. At a magnification of 10,000, only one-four hundredth of one of these openings is viewed. Methods of mounting consist of dispersing carbon in nitrocotton by the Coblac method[1], atomizing on

* Reprinted from *The Rubber Age* (New York), Vol. 50, No. 12, pages 431-436, March 1942. This paper is a condensed version of a paper presented before the Buffalo Rubber Group of the Division of Rubber Chemistry, American Chemical Society at Buffalo, February 27, 1942.

a prepared mesh screen, or dispersing on a film by means of a high frequency electric discharge[2].

The first photograph of carbon appeared in *Electronics*, November, 1938. This photograph, taken with the first German instrument by Siemens, showed particles of carbon deposited by a candle flame, which were described as "small hexagonal scales."

In July, 1940, the Columbian Carbon Company, reported[3] the particle size of Micronex as 28 millimicrons, and revealed the shape of these colloidal carbon



Micronex (32,400x).

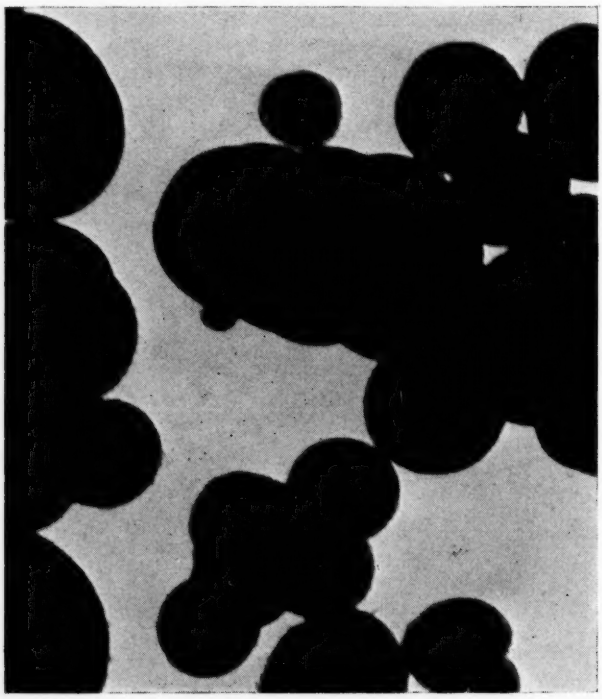
particles as spheroidal. In addition, for the first time, distribution curves were used to obtain accurate mean particle-diameters and surface areas of colloidal carbon.

As late as January, 1941, the Germans still claimed hexagonal or circular platelet form for carbon particles[4]. Schoon and Koch based this claim on stereoscopic photographs of a few carbons. Later, however, in May, 1941, Heering, Gizycki and Kirseck[5] showed the form of Thermax and P-33 to be spheroidal, thus fully substantiating the results of the Columbian Carbon Company's previous work in 1940.

Measurements of particle size are most conveniently made on a print enlarged to 50,000 diameters. Only particles that are discrete or reveal a full diameter are measured. From these values, distribution curves are plotted. These give the

number of particles (expressed as a frequency percentage) for each particle-diameter range. Skewness in the curves is due either to inability to discern very small particles (Super-Spectra) or to a wide and unsymmetrical range of particle sizes (lamp black).

The distribution curves provide the only means for determining the true mean diameter of carbon particles and, hence, accurate surface areas. The correct method for obtaining accurate surface values would be to sum up the areas of the individual particles. Assuming a symmetrical distribution curve, however, a very close approximation to the correct value can be readily calculated. Errors by other methods are also discussed in the original Columbian publication[3].



Thermax (50,000x).

THE ROLE OF SURFACE IN REËNFORCEMENT

This subject has been discussed in a recent communication[6]. The preliminary conclusions may be summarized as follows:

(a) Energy of rupture (resembling tinting strength) is dominated by surface area up to 8 acres, thereafter tending to flatten out.

(b) Tensile strength (like color) shows continued upward trend with surface area.

(c) Modulus (at 300%) presents little discernible response to increasing surface.

(d) Hardness (Shore) displays a generally upward trend with increasing carbon surface, and raw plasticity a corresponding downward trend.

(e) Electrical conductance shows no consistent trend with advancing surface area.

(f) Rebound resilience alone appears to correlate consistently downward with increasing surface.

ANOMALIES AND THE NEED FOR A NEW THEORETICAL APPROACH

Acetylene black and lamp black are lower than expected in energy of rupture, tensile strength, tinctorial strength, plasticity and density, and higher than expected in modulus, hardness, electrical conductivity, sedimentation volumes (Figure 1), thixotropy coefficient (Figure 2), and absorption. This anomalous

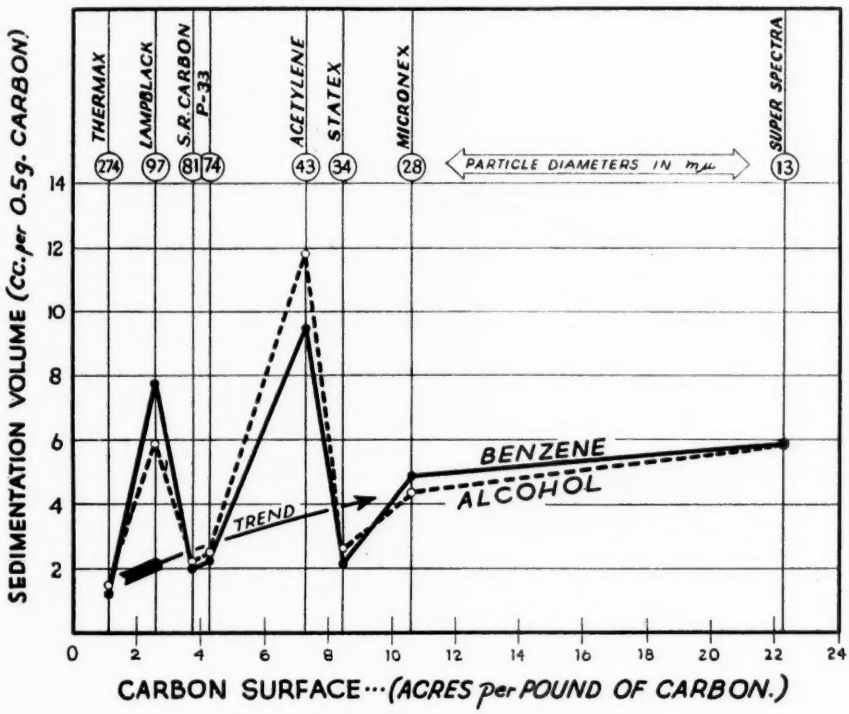


FIG. 1.—Colloidal behavior of rubber carbons.

behavior is ascribed to the presence and persistence of carbon-to-carbon complexes or networks, which impede, by competition, the reënforcement reaction, at the same time raising all consistency (absorption) values.

The subnormal properties of thermal carbons with respect to modulus, hardness, sedimentation volume, absorption, and, in particular, bound rubber, are regarded as due to complete inertness; *i.e.*, total absence of either carbon: carbon, or carbon: rubber, complexes.

REBOUND RESILIENCE AND SURFACE AREA OF CARBONS

In Figure 3 this curve is assigned a tentative trend based on a foundation of electron microscope determinations, interspersed with other surface values de-

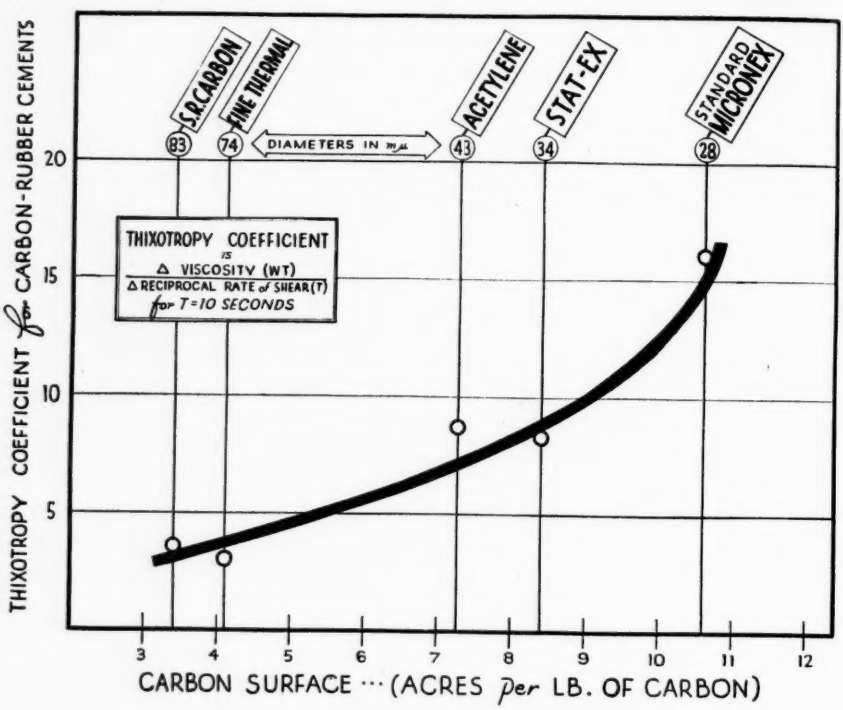


FIG. 2.—Colloidal behavior of rubber carbons.

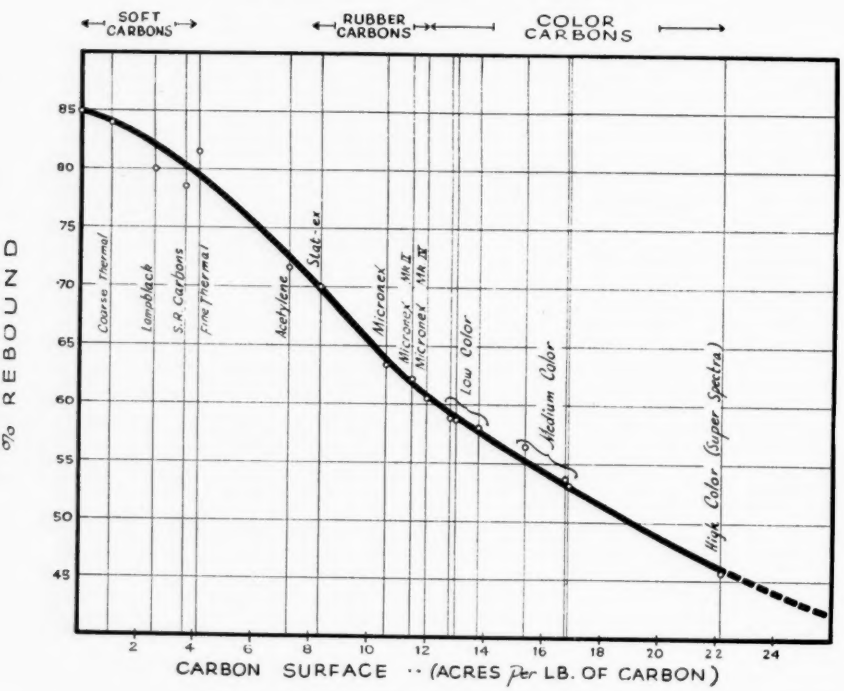


FIG. 3.—Rebound resilience and carbon surface.

rived from color measurements. The examination of any new carbon may well begin with a determination of its resilience properties by means of the Healey-Goodyear pendulum. This will serve to fix its general position in the surface-area scale, and so the broad features of its hysteresis and processing properties.

There appears, at least in this tentative curve, a point of inflection in the region of rubber-grade impingement carbons. A slight reduction in carbon surface area at this point is repaid by a marked increase in rebound resilience and concomitantly by decreased hysteresis and heating tendencies under dynamic stresses. The 8-acre point (Statex) appears, in the light of present knowledge, to combine a surface area which, being almost completely available (in rubber), provides full reënforcement and road wear, with a higher degree of resilience or freedom from hysteresis than has hitherto been obtainable.

The advisability of any further shift towards still lower surface-area carbons depends, of course, on the relative importance of low hysteresis and full reënforcement. This will, in turn, be governed by service conditions and by the inherent properties of the rubber itself—natural or synthetic.

To portray these relationships more concretely, an attempt has been made to evaluate tread quality under three sets of conditions. The indexes used are somewhat arbitrary, the objective being to fix ideas.

OVERALL QUALITY AS A FUNCTION OF CARBON SURFACE AREA (FIGURE 4)

Road wear (*energy of rupture and Shore hardness*).—The product of these two quality indexes is regarded by some as the best criterion of abrasion resistance or road wear. Energy of rupture measures overall reënforcement. Shore hardness determines the freedom from excessive crawl or squirm[7], which appears to be a *sine qua non* of maximum road wear.

This index indicates a rapid rise from low surface areas up to about the 8-acre point, thereafter a slight but continued rise to 12 acres (and probably beyond). The end point of this curve has not been established. It is suggested that this index broadly depicts road wear performance under nonheating conditions, as, for example, passenger tires driven at low speeds. The unexpectedly low values for fine thermal and acetylene blacks are ascribed to the absence of carbon: rubber bonding and the competition of persistent carbon: carbon complexes, respectively.

Heavy-duty performance (*energy, Shore hardness and rebound*).—This index differs from the previous one in that the rebound-resilience factor is added. The resulting values represent a compromise between abrasive wear and the conditions induced by excessive speeds, or loads, or both. A maximum or optimum point appears in the 8-acre region. This optimum will shift to the left or to the right, depending on the relative importance ascribed to the wear factor, *per se*, and to low power losses (high rebound resilience). This curve is essentially schematic. Road tests on large truck tires have, however, confirmed the superior performance of a new type of carbon in the 8-acre range.

Electrically conducting tread quality index (*energy, Shore hardness, rebound, and conductance*).—This index adds to the previous one the factor of d. c. conductance. An absolute maximum appears in the 8-acre region for a pure carbon (Statex), but two subregions are discernible. In the pure-carbon range, increasing surface provides increasing quality, fine thermal carbon displaying a downward anomaly. Among the impingement carbons, there is again a rise in quality with increasing surface. The sharp drop from Statex to standard carbon black is due to the appearance of volatile substances in the latter. This drop occurs

despite a rise in surface from 8 to 12 acres. The curve illustrates the contribution of the two chief controlling factors in the development of nonstatic tread carbons, *viz.*, purity and fineness of subdivision.

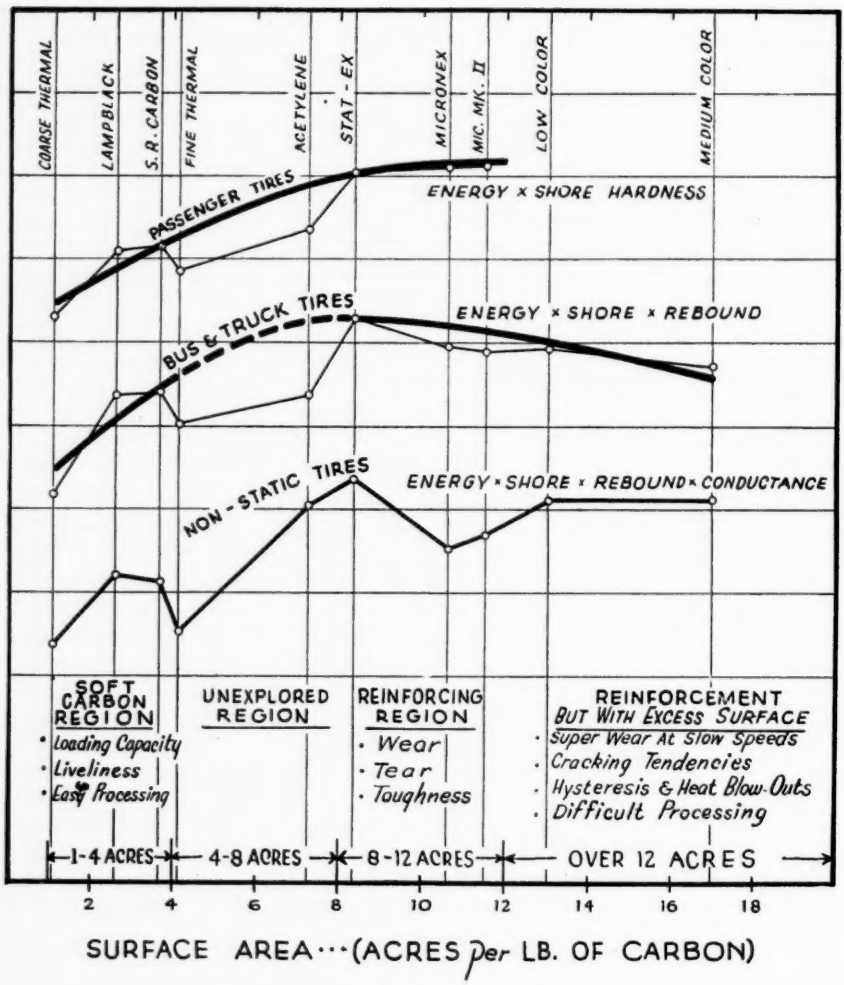


FIG. 4.—Carbon surface and tread quality.

The attainment of electrical conductance through the use of excessively high surface channel carbons incurs the penalty of high hysteresis and difficult processing.

THE GAMUT

Inspection of Figure 4 suggests the following broad classification of colloidal carbons available for rubber compounding.

(1) *One to four acres—Soft carbon region.*—Here, at the price of low reënforcement are found the outstanding advantages of easy processing, high loading capacity, and liveliness.

(2) *Four to eight acres—Terra incognita.*—In general this region may be described as the unexplored area in the colloidal carbon "spectrum." Although in this range, acetylene black, is not deemed a true rubber carbon because of its anomalous behavior.

(3) *Eight to twelve acres*—The reënforcing region.—Here are found Statex and standard reënforcing carbons which impart wear, tear, and toughness to rubber and which have made possible the superquality tires of today.

(4) *Upwards of twelve acres—Reënforcement with excessive surface.*—In this region a slight improvement in abrasion resistance over (3) is purchased at ever-increasing cost in hysteresis, difficult processing, and boardiness.

Shepard, Street, and Park[8], writing in 1937, stated: "It has been pointed out that data are lacking which make it possible to determine whether fineness of division alone produces reënforcement. This problem is one of the most difficult; but if solved, it would throw great light on the whole question of reënforcement."

With the aid of the electron microscope, it is now possible to attempt an answer. Gaps in the carbon "spectrum" may now be recognized. The next step is to fill these gaps, so that a complete range of colloidal carbons, from one to twenty acres or more, may be made available.

So equipped, and with access to a chemically controlled carbon surface, the rubber technologist will be better able to meet every problem of reënforcement, loading capacity, or processing behavior, whether working with natural rubber or with other elastic polymers.

REFERENCES

[1] Columbian Carbon Co., U. S. patent 1,987,980.
[2] Developed by A. Prebus, Ohio State University.
[3] "The Particle Size and Shape of Colloidal Carbon as Revealed by the Electron Microscope", July **1940**; RUBBER CHEM. TECH. **14**, 52 (1941).
[4] Schoon and Koch, *Kautschuk*, January **1941**.
[5] Heering, Gizycki and Kirseck, *Kautschuk* May **1941**.
[6] Wiegand, *Can. Chem. & Process Ind.* **1941**, 579.
[7] The authors are indebted to W. W. Vogt of The Goodyear Tire & Rubber Co. for this apt descriptive term.
Shepard, Park and Street. in "The Chemistry and Technology of Rubber", Edited by Davis and Blake, Reinhold Publishing Corp., New York, **1937**, p. 410.

THE ESTIMATION OF SMALL PERCENTAGES OF RUBBER IN FIBROUS MATERIALS *

C. M. Blow

Laboratories of the British Rubber Producers' Research Association, Welwyn Garden City, Herts., England

Rubber is being used in increasing quantity in fibrous materials of all types as a binder or to impart particular and special properties. The percentage of rubber employed varies from 3 to 15 or 20 per cent, and it is becoming of interest and importance to have analytical methods to estimate with some degree of accuracy the percentage present. This estimation has several difficulties, and no one method can be adopted on account of the difference in behavior of various fibres.

The fibre may consist of protein, such as silk, wool and other animal fibre, leather, or cellulose, such as jute, cotton, rayon, paper, kapok, etc. The rubber may be vulcanized or unvulcanized, and partly or completely in the oxidized state. In addition, there may be organic material, such as protein, soap (added as stabilizer for the latex), fats, oils, waxes, dyestuffs and inorganic substances from the fibre, fillers and pigments, coagulants, and so forth—to name only a few possible compositions. The problem appears complex, but may be simplified in some cases by knowing, from the process of manufacture, the definite absence or presence of certain of these likely ingredients.

It is well first to tabulate the various techniques that appear open to us:

1. The use of solvents to remove the rubber without affecting the fibre. The percentage extract or percentage loss in weight of the material may be determined.
2. Destruction of the fibre by a chemical reagent which is without effect on the rubber.
3. Oxidation, or, more generally, chemical modification, of the rubber to render it more readily removable from the fibre by extraction with a solvent or by emulsification with a detergent.
4. Quantitative reaction of a chemical reagent with the rubber.

Each of these first three methods has its application, and will be discussed in detail. In the first place, we shall confine the discussion to a simple mixture of fibre (of one type) and vulcanized or unvulcanized rubber.

1. *The use of solvents to remove the rubber without affecting the fibre.*

One of the established methods for the removal of a coating of rubber from cotton fabric, *e.g.*, mackintosh, is to reflux the material with nitrobenzene and wash with solvent. For a discussion of this and a modified method, reference may be made to a recent paper by R. A. Hublin (Rubber Chemistry and Technology **13**, 931(1940). This author suggests the use of *o*-nitroanisole as an alternative, and details a method as follows. The material is refluxed with *o*-nitroanisole for 30 minutes at 115° C. After cooling, a mixture of carbon tetrachloride

* Reprinted from the *India-Rubber Journal*, Vol. 102, No. 37, pages 719-722, March 14, 1942.

and toluene is added, and the undissolved nonrubber components are recovered by filtration and weighed.

Simple rubber solvents, such as benzene, petrol, and carbon tetrachloride, are not reliable, since vulcanized rubber only swells in such solvents, and would not be completely extracted; even unvulcanized rubber is not always completely removed.

This technique is not generally adaptable to small quantities of rubber, and suffers from the disadvantages that it is slow, that it requires considerable apparatus and volumes of solvents to handle any number of analyses, and that there is a fire hazard with nitro solvents. Nevertheless, the latter have been, and are used, with success for gross amounts of rubber.

2. *Destruction of the fibre by a chemical reagent without effect on the rubber.*

This method is applicable to protein, which is destroyed by boiling caustic soda, a reagent that does not affect rubber to any measurable extent.

The general method is to boil the weighed sample (1-2 grams) in about 30 cc. of 5 per cent caustic potash or soda (a 1 per cent solution for a longer time is recommended by some workers) until the fibre is completely destroyed (normally 10-15 minutes), separate the rubber, dry and weigh it. Separation of the rubber sometimes presents difficulties. In the case of, say, a white woollen or worsted yarn, it is not usually difficult to filter the caustic soda solution through a No. 4 filter, *e.g.*, in a Gooch crucible with gentle suction, wash, remove from the paper as a pellet, and dry.

Low quality woollen, *e.g.*, carpet, yarns and heavily dyed materials, are often difficult or impossible to filter on account of finely divided gelatinous substances and(or) dyestuff. The method adopted is to centrifuge the caustic soda solution in a hand centrifuge, whereby the rubber rises to the surface and the nonrubber components sink. Both top and bottom layers are washed once or twice, and recentrifuged to ensure complete separation. The rubber can usually then be easily collected, dried and weighed.

Potassium or sodium hydroxide devulcanizes vulcanized rubber to some extent, but this does not upset the quantitative value by more than a small percentage of the rubber. Oxidized rubber is dissolved, or at least finely dispersed, and does not appear in the rubber figure.

The same technique can be applied to leather-rubber compositions and real silk containing rubber, without any difficulties not encountered and dealt with above. A similar technique for cellulosic material, however, presents great difficulty practically.

A number of "solvents" for cellulose have been tried, but the high viscosity makes separation of the rubber difficult, particularly as the rubber may be in a fine state of division. The only method that appeared at all promising was to use boiling concentrated hydrochloric acid to break down the fibre structure. Using 1-2 grams of material, it was found that, if the hydrochloric acid was decanted off through a sintered glass or Alundum crucible and the slurry of degraded fibre and rubber was shaken up with 50 cc. of water and 10 cc. of benzene, the rubber (even if vulcanized) appeared in the benzene layer, and the cellulose material could be separated off. Finally, the rubber was precipitated from the benzene by means of acetone and filtered and weighed. Oxidized rubber again does not appear in the rubber figure, as it is dissolved by the acetone.

It is advisable in this method to add a small amount of oil-soluble dye to the benzene, if the rubber is not already dyed or pigmented, to make separation easier.

This method has been found satisfactory only for a good-quality cotton yarn containing up to 10 per cent of rubber. It is not simple, and some practice is necessary to judge the optimum amount of boiling, temperature to filter, and so on.

3. *Oxidation or, more generally, chemical modification of the rubber to render it more readily removable from the fibre by extraction with a solvent or by emulsification with a detergent.*

The difficulty of destroying cellulosic material without affecting rubber throws one back to the need for extraction of the rubber by some means. As stated above, solvents are not satisfactory, and some other method was sought. Modification of the rubber to make it more readily removable from the fibre suggested itself, and oxidation appeared the most promising.

It may be pointed out here that textile material takes up water in a proportion related to the atmospheric humidity, and since this socalled regain may range from 0-20 per cent, this is an important point. Drying of all textile material at 90-100° C for 1-2 hours and weighing in closed vessels is perhaps the most satisfactory technique, the textile material, after removal of rubber, being similarly dried before weighing. Alternatively, all weighing may be carried out in an atmosphere of controlled temperature and relative humidity.

Oxidized rubber, as stated, is dispersed or even soluble in caustic alkali and is soluble in acetone; and, furthermore, it has been shown that it is readily and completely removed from textile material by a simple soap and soda scour.

The following table gives confirmatory evidence of these facts in the case of a woollen fabric. The small acetone extract of oxidized, scoured fabric arises probably from residual soap. The acetone extract in the case of oxidized, unscoured fabric is large on account of oxygen absorbed.

RUBBERIZED WOOL FABRIC

(Untreated)	(Scoured)	(Oxidized in air—Cobalt catalyst)		(Scoured)	
R.C. (NaOH)	R.C. (NaOH)	R.C. (NaOH)	A.E.	R.C. (NaOH)	A.E.
4.8	4.9	Trace	5.72	Trace	1.10

Rubber can be oxidized by exposure to air at elevated temperature or to sunlight (or its equivalent—Fugitometer) for a period of time which varies considerably. To catalyze and accelerate oxidation, addition of a metal salt, such as cobalt or copper linoleate or naphthenate is employed with great advantage. To replace air by hydrogen peroxide or other recognized oxidizing agent is an obvious step.

When we come, then, to work out a method of analysis based on this principle, we have a large number of possible techniques, all of which, however, consist of the following three well-defined stages.

(*a*) Incorporation of the catalyst.

This may be, as stated, cobalt or copper naphthenate, linoleate or stearate, applied either as a dilute solution in carbon tetrachloride or benzene, or as a dilute emulsion in alkali, *e.g.*, ammonia; 1-2 per cent of the catalyst by weight on the dry material is required.

The following is a formula for a suitable emulsion:

Cobalt linoleate	10 g.
Sextol	20 cc.
Ammonia (1 per cent)	20 cc.
Vulcastab LS (1 per cent)	5 cc.

Diluted to 1 liter for use.

(*b*) Oxidation of the rubber.

If the material is finely divided and air can be made to reach all the surface readily, oven heating at 70° C for 1-2 hours is usually sufficient for complete oxidation in the presence of the catalyst.

As an alternative, hydrogen peroxide appears the best oxidizing agent to use, since it leaves no residue to complicate subsequent determinations. The rubber-containing material can be steeped in 20-40 times its weight of 3-5 vols. H_2O_2, warmed to 50-60° C, and maintained there for 15-30 minutes, and then, if necessary, filtered or evaporated to dryness before passing to the next stage.

(*c*) Separation of the fibre from the oxidized rubber.

We have two alternative methods.

First, as stated above, the oxidized rubber can be removed by boiling either with 1-2 per cent caustic soda solution or with dilute sodium carbonate solution (0.1-0.2 per cent), with or without the addition of a small proportion of sodium oleate. The fibre (the rubber having been oxidized and dispersed) can be then collected, washed, dried, and weighed. Whether sodium hydroxide or sodium carbonate is used depends on the fibre involved.

Alternatively, the oxidized rubber can be extracted with acetone, after which the fibre or the extract can be weighed. It may be pointed out here that, provided due attention is paid to the moisture content of the fibre, it is preferable to confine one's weighings to the fibre, since the rubber contains a rather indefinite percentage of oxygen. From blank determinations carried out, it appears that slight oxidation of the cellulose occurs by treatment with cobalt linoleate and hydrogen peroxide, resulting in a loss in boiling caustic soda of approximately 2 per cent. This is one point in favor of acetone extraction of the oxidized rubber.

Reaction with a halogen as an alternative to oxidation has suggested itself, but has not yet been fully investigated. One difficulty is the reactivity of certain fibres with the halogens.

4. *Quantitative reaction of a chemical reagent with the rubber.*

This suggestion was looked into thoroughly, and some experimental work was carried out. It appears that the only method likely to achieve practical success is to employ a carbon tetrachloride solution of a halogen (bromine appears most suitable) to form the tetrahalide of the rubber, the excess being liberated as iodine by potassium iodide and titrated with thiosulfate.

The experimental results of the investigation are as follows.

The product is finely divided and dried at 80-100° C, and 1-gram portions are immersed in 50-100 cc. of a carbon tetrachloride solution of bromine containing 50 per cent more bromine than is expected to be required for the reaction. The reaction is allowed to take place at room temperature, with occasional shaking or stirring in a stoppered flask. After times ranging from 30-120 minutes, a solution of potassium iodide is added, and the liberated iodine is titrated with sodium thiosulfate, in the presence of starch.

The following figures are the mean of 8-10 determinations, and the percentage of rubber was calculated on the assumption that the tetrabromide is formed. A worsted yarn was treated with vulcanized and unvulcanized rubber for this work.

Applied	Percentage of rubber found: Vulcanized rubber	Percentage of rubber found: Unvulcanized rubber
2% rubber	1.2	1.8
4% rubber	2.65	4.0
6% rubber	4.2	7.3
10% rubber	7.1	12.0

Control figure on unrubberized wool equivalent to approximately 0.4 per cent rubber was corrected for in all cases.

In view of these results, this line of attack has been dropped.

* * * *

The product for analysis is rarely a simple mixture of fibre and rubber. A comprehensive list of possible other substances has been given above.

Experimental.—The material to be analyzed should be as finely ground or cut as possible. It is essential to extract it with acetone before any determination. Acetone removes oils, fats, much of the waxes and organic dyestuffs, and oxidized rubber, but does not affect rubber—vulcanized or unvulcanized. When a soap and soda scour or caustic soda treatment is to be part of the determination of the rubber content, an alkaline-water extraction is also necessary; protein, soaps, soluble coagulants, starches, etc., are removed by this.

In the case of rubber destruction methods, separation of the fibre from emulsified oxidized rubber may present problems. It is advantageous to centrifuge the solution to separate the fibre, which is subsequently washed in the centrifuge, and then filtered. This latter separation can often be carried out in a Gooch crucible, using the fibre to form its own filtration pad. The fibre, after drying and weighing, is checked for purity by an ash determination. When the oxidized rubber is to be estimated by acetone extraction, the fibre can be filtered direct into a thimble.

The acetone- and water-insoluble nonfibre and nonrubber components appear in the rubber in the case of fibre destruction methods and, therefore, the purity of the rubber must be checked by ash determination.

Corrections for added cobalt or copper salt must be made.

By way of illustration of the methods described above, the following brief notes and specimen results are added. They cover three main types of analysis. In all cases the first operations are comminution and acetone extraction. Percentages are based on the weight of the oven-dried material; 1-1.5 grams is taken for each determination.

1. Rubberized Wool Yarn, Fabric or Felt: Reconstituted Leather Board (Containing no Cellulose)

	Wool yarn %	Leather board %
(*a*) Acetone extract	1.9	15.0
(*b*) Acetone-extracted material boiled in 5% caustic soda, until fibre structure is destroyed. Rubber separated from other residues centrifugally, washed dried, and weighed	8.3	18.5
(*c*) Rubber ashed—weight	0.1	3.5
Rubber by difference	8.2	15.0

2. Rubberized Cotton Yarn or Fabric: Paper or Millboard Containing Rubber

	Cotton yarn %	Cellulose board %
(*a*) Acetone extract	2.1	7.9
(*b*) Acetone-extracted material boiled in 2% caustic soda, filtered, dried and weighed	95.5	—
(*c*) Acetone-extracted material treated with 2 cc. of 1% cobalt linoleate solution, dried; warmed with 50 cc. of 3-vol. hydrogen peroxide at 70° C for 30 minutes:		
(1) After addition of 50 cc. of 2% caustic soda, boiled, filtered, and weighed	80.3	—
Fibre ashed—weight	0.5	—
Rubber by difference	15.2	—
or (2) Filtered into paper thimble, and extracted with acetone. Weight of extract (rubber)	—	9.0

3. Imitation Leather (Containing Leather Waste, Cellulose and Rubber)

	%	%
(*a*) Acetone extract	—	7.2
(*b*) Acetone-extracted material boiled in 100 cc. of 1% caustic soda, filtered, dried, and weighed	58.7	—
Fibre ashed-weight	7.0	51.7α
(*c*) Acetone-extracted material treated with 2 cc. of 1% cobalt linoleate solution, dried; warmed with 50 cc. of 3-vol. hydrogen peroxide at 70° C for 30 minutes:		
(1) After addition of 50 cc. of 2% caustic soda, boiled, filtered, and weighed	49.7	—
Fibre ashed—weight	5.1	44.6β
or (2) Filtered into paper thimble, dried, extracted with acetone. Weight of extract (rubber)	—	6.6
Fibre boiled with 100 cc. of 1% caustic soda, filtered, and weighed	50.9	—
Fibre ashed—weight	6.6	44.3β^1
(*d*) Original material ashed—weight	—	10.3

$\left(\alpha - \frac{\beta+\beta^1}{2}\right)$ gives a rubber content of 7.2 per cent compared with 6.6 per cent by extraction. Alkali-soluble substances, including leather, 34.1 per cent by difference.

It is realized that this paper suffers from a certain incompleteness, but time has not permitted a full investigation of all the types of products, nor the development of the several refinements that will arise from experience of the techniques.

ACKNOWLEDGMENT

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STATIC ELECTRIC PROBLEMS IN TIRES *

J. W. LISKA and E. E. HANSON

Firestone Tire and Rubber Company, Akron, Ohio.

Since its advent about thirty years ago, the pneumatic tire has been remarkably improved to meet increasingly severe requirements. Improvements in motor vehicles, increased speed of travel and, in general, a more and more critical attitude on the part of the consumer, have introduced difficult problems for the rubber technologist. One of the more recent and unusual of these problems, introduced in part by the popularization of the automobile radio, has been the accumulation of static electrical charges on a moving car.

At first difficulty was experienced mainly with radios in passenger cars. In some cases when the auto was stationary and the motor running, the program reception was clear and uninterrupted but, when the car was set in motion and driven for some distance, reception was seriously impaired by loud, intermittent static noises.

Later, reports began to circulate of toll-bridge collectors receiving severe electrical shocks on touching any part of a car which had just pulled to a stop after a sustained drive. Similar phenomena reportedly took place when motorcycle police touched cars they had pursued and stopped. Recently, passengers on commercial busses, especially on those operating in hot, dry regions, have experienced electrical shocks on entering or leaving.

The object of this paper is to describe some of the methods employed in measuring, and some of the means developed for controlling, the observed effects.

AUTO RADIO INTERFERENCE

The first experiments were made to determine whether the tires were actually causing the static discharge which was interfering with radio reception. A radio-equipped car which was reported to have given some trouble was obtained, and the observations recorded in Table I were made. These tests proved conclusively that the static developed was caused principally by the tires, and was in no appreciable degree connected with the ignition system of the car or the air stream around it.

Item 6 in Table I gave a clue to the mechanism or source of static discharge, and led to a rather simple and effective method of reducing this type of static trouble. The results indicated that, when the wheels were connected electrically through the brake bands to the frame of the car, the static discharge diminished considerably. After the brakes were released, if the car still had sufficient speed, the static discharge again built up to annoying proportions.

The following mechanisms appears to explain the observations given in Table I. Charge separation occurs in the tire-pavement contact area by the familiar "frictional" process[15]. This is possible because the tire tread, and usually the road surface, are poor electrical conductors. However, a tire is not a perfect insulator.

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 34, No. 5, pages 618-624, May 1942. This paper was presented before the Division of Rubber Chemistry at the 102nd Meeting of The American Chemical Society, Atlantic City, September 12, 1941.

Therefore the charges on the tread leak over and through the tire side walls to the wheel. A leakage also occurs from the wheel to the pavement contact area. If we assume that the car moves at a constant velocity over a uniform pavement, an equilibrium will eventually be reached between the charge leakages from the treads to the wheels and from the wheels to the pavement contact areas.

However, since pavement surfaces usually do not possess uniform electrical properties, the rate of charge generation at the tire treads of a moving car fluctuates over wide limits, and the equilibrium voltage is frequently interrupted. Because the rear wheels are connected electrically to the frame of the car, they possess a much larger capacitance than the front wheels, which are partly insulated from the frame by grease films in the bearings. It is, therefore, likely that large enough differences of potential often exist across the grease films in the front wheel bearings to cause electrical breakdown. Another, and possibly more important, cause of radio static from tires is the charging of the car by induction. The negatively-charged tire treads repel electrons from the fenders and other nearby regions to the more remote parts of the car and, in general,

TABLE I

ORIGIN OF AUTO RADIO INTERFERENCE

Operating conditions	Radio interference
1. Motor idling, car stationary.	No static.
2. Motor racing, car stationary.	No static.
3. Car being driven slowly.	No static.
4. Car being driven over 40 m. p. h.	Gradually increasing amount of static.
5. Car coasting down hill at 40 m. p. h. after being driven for several miles at or over 40 m. p. h.; motor turned off.	Undiminished static until car speed was reduced.
6. Sudden, short-duration application of brakes (after development of steady static interference).	Momentary reduction of static.
7. Condition 4 with another set of tires.	Considerably less static than for condition 4.

lower its potential with respect to the ground. Whenever a fluctuation in the tread potential occurs, momentary electrical displacement currents also occur in the car. Any insulation between various parts of the car, such as the grease film in the front-wheel bearings, will therefore be conducive to sparkover. This process probably is responsible for the major part of tire static interference with radio reception.

This theory is substantiated by the fact that, if the axle and the wheel are maintained at the same potential by small coil springs placed in compression between the metal hub of the front wheel and the front axle, the greatest part of the static trouble is eliminated. What little remains is not troublesome, and can probably be ascribed to a similar mechanism between other fairly well insulated parts of the car.

Comparative tests were next undertaken in an attempt to measure the potential differences developed between the car body and ground. In these tests a long, link chain, insulated from the car body, was pulled along the ground behind the car. The high-voltage terminal of an electrostatic voltmeter was connected to the chain, and the other terminal was connected to the car body. It is admitted that some charge separation took place between the chain and the road. However, since it was found that the potential generated by the chain

was small in comparison with that generated by the tires and was quite constant, no explicit correction was made for this part of the observed potential. Another method was also employed. Voltages on both stationary and moving cars were measured by touching the cars with a probe connected to an electrostatic voltmeter stationed at the side of the road. For a moving car, these measurements recorded only the voltage at the moment of contact; for a stationary car they indicated the voltage on contact and its subsequent decrease. The chain technique, used with a short-period portable electrostatic volmeter, had the advantage of permitting measurements of voltage to be made continuously during operation of the car. Some typical data obtained by this method follow:

Set of tires	Voltage between car body and ground
A	1000
B	1700
C (reported to produce serious static interference)	5200

The car potential was found to be affected greatly by atmospheric conditions and by the type of pavement. On a smooth asphalt pavement much more static was observed than on a concrete pavement. The car potential for a given pavement increased with decreasing humidity. When the car was driven at 30 miles per hour (on a concrete pavement), the potential was usually below 1000 volts for a humidity over 50 per cent; but under the same conditions, on an asphalt pavement, the potential might be as high as 3000 or 5000 volts. It was also found that the potentials generated on the car were lowest in the morning and gradually increased during the day, even when no appreciable changes in humidity and air temperature occurred. This increase in static production was probably due to a progressive drying out of the road surface as road temperatures increased. Over as small a distance as 0.5 mile on a uniform pavement, fluctuations in the car potential as large as 1000 or 2000 volts were often recorded. These observed fluctuations lend support to the previously mentioned theory that radio static depends on fluctuations in the rate of charge generation by the tires.

These preliminary road tests demonstrated that a definite difference in the static generating properties of various sets of tires existed. Because the evaluation of a long series of experimental tread stocks on the basis of such road tests was impracticable from the standpoint of both time and cost, the development of a method of laboratory evaluation was desirable.

Several methods of simulating the wiping action of a tire tread on a road surface were tested. The most successful of the laboratory units developed is shown in Figure 1. The rubber test slab, $0.635 \times 12.7 \times 12.7$ cm. ($0.25 \times 5 \times 5$ inches), is placed in a flat holder connected by a set of four links (to prevent rotation of the slab) to a set of fixed, insulated pegs. This system, in turn, is supported on a lifting mechanism which permits the slab to be raised from or lowered into contact with a rotating disk. A steel ball is embedded in this disk near its outer edge so that, as the disk rotates, the ball slides along the surface of the rubber slab in a circle. A metal box enclosing the mechanism acts as an electrostatic shield which prevents stray charges or fields from affecting the electroscope system.

Reasonably reproducible results could be obtained only by observing certain precautions. For instance, the surface of the test slab had to be carefully buffed before each test-run. Because atmospheric conditions were found to affect the

results seriously, it was necessary to make measurements on a control sample for every group of tests.

In operation, the slab holder was elevated from contact with the disk, and a carefully prepared slab was put in place. The assembly was then lowered so that the test-piece rested on the disk and the entire system was grounded. The motor was started and run until the electroscope indicated that a constant, maximum potential had been reached. The motor was stopped, the holder raised,

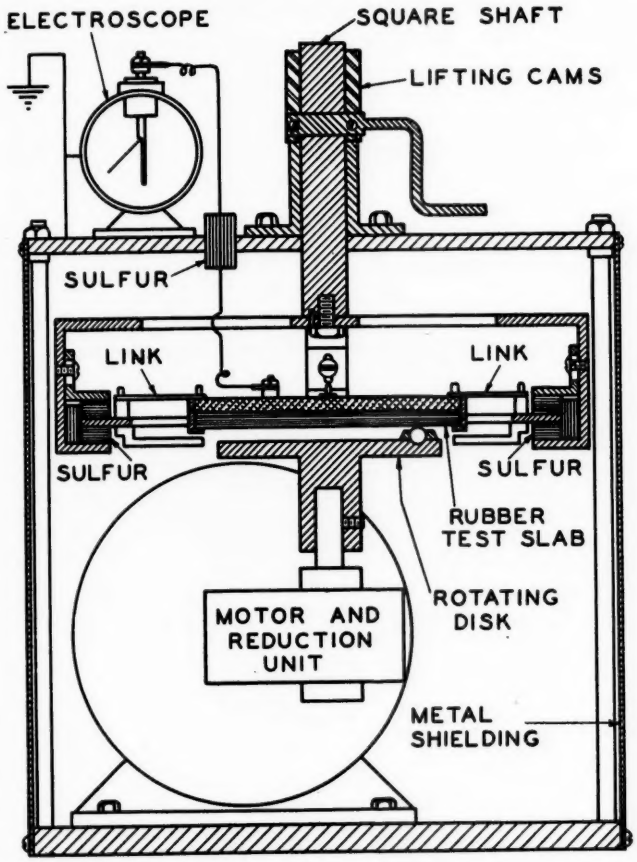

FIG. 1.—Friction type static machine.

and, after removal of the test piece, a new one was installed and the process repeated. The results of some of the tests to determine the effect of various compounding ingredients on static generation are shown in Figure 2.

In much of the previously published work[4-13] on generation or production of static charge by one means or another, considerable emphasis has been placed on attempts to formulate an "electrostatic" series for materials, similar to the familiar electromotive series for elements. As a result of some experiments on so-called contact electrification, Coehn[2, 3] derived the expression (now generally known as Coehn's rule):

$$Q = C(E_1 - E_2)$$

This states that, if any two dielectrics are placed in intimate contact and later separated, the electrostatic charge separation is directly proportional to the difference between the dielectric constants of the two materials. It states further that the substance having the higher dielectric constant always become positively charged. Under certain conditions and with certain materials, fairly quantitative confirmations of this rule have been reported[8].

Preliminary measurements of dielectric constants of stocks whose static generation was known failed to show any positive correlation. Furthermore, these tests indicated that the experimental technique necessary to obtain consistent results was quite involved.

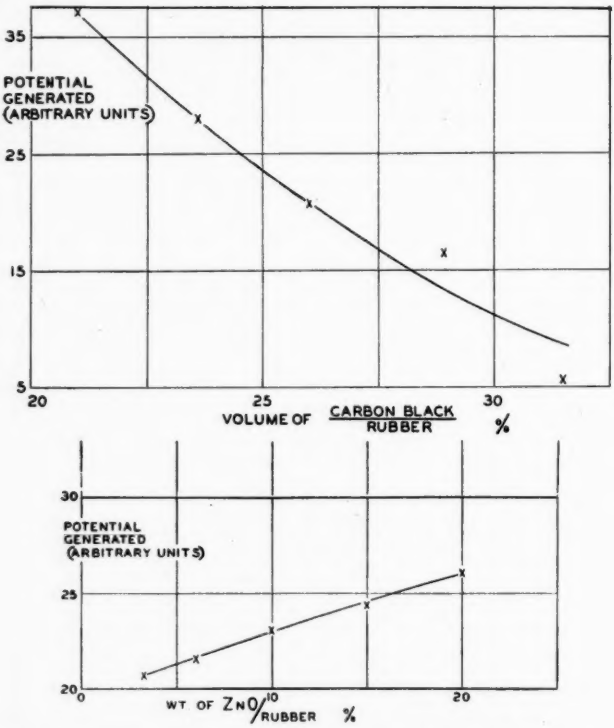

FIG. 2.—Static generation *vs.* carbon black and zinc oxide loading.

In an attempt to obtain a simpler means for evaluating the static-producing properties of tire stocks, a method of resistivity measurement was developed, since resistance is an important factor in static generation. Preliminary resistivity tests on all of the stocks tested in the static machine showed that, in all cases of relatively low resistivity, a low rate of static generation also existed. A few cases of low static generation, together with relatively high resistivity, were found, but, because of the simplicity and ease of obtaining resistivity measurements, many of the later tests were made by the use of this technique.

A schematic diagram of the circuit used for the conductivity measurements is shown in Figure 3. The potential source, V, was either a set of dry cells or a

rectifier providing a voltage which could be varied from about 500 to 1000 volts. The electrode system, *S*, consisted of a set of 0.32-cm. (0.125-inch) polished-brass plates so arranged that the distance between the guard ring, *g*, and the central electrode, *C*, was 0.48 cm. (0.188 inch). To assure good electrical contact between the brass plates and the samples, the electrode surfaces of the samples were painted with Aquadag. The surface of the sample in contact with the guard-ring system was painted with the aid of a template so that a strip about 0.48 cm. remained unpainted between the central electrode and the guard-ring. The size of the rubber samples was $5.08 \times 7.62 \times 0.25$ cm. ($2.0 \times 3.0 \times 0.1$ inch) and the central electrode size was 2.54×5.08 cm. (1.0×2.0 inches). A spotlight galvanometer, *G*, with a sensitivity of 2.2×10^{-8} ampere per mm., was used to measure the current.

The electrical resistivity was found to correlate fairly well with the results from the previously described friction-type static machine:

Sample	Potential generated (arbitrary units)	Resistivity (megohm-cm.)
A	16	42
B	31	57
C	78	123
D	172	125
E	275	833

Therefore the resistivity measurements provided a rapid method for choosing those stocks which would be most likely to give low static voltages when used in tires. Actual road tests or indoor drum tests were then made on these tires.

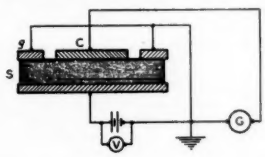

FIG. 3.—Wiring diagram for resistivity measurement.

It was found that the electrical resistivity of a rubber compound varied with its strain history subsequent to curing. For example, a single 50 per cent elongation increased the resistivity of a sample by as much as a factor of 100. The resistivity approached its original value, depending on the length of the subsequent rest period. This characteristic increase in resistivity on flexing, followed by partial recovery on resting, is sometimes retained by the stock until complete failure by flexing. The effect of flexing is shown in Figure 4. The data were obtained from measurements on strips of rubber which were stretched manually and, also, by a flexing machine to 50 per cent elongation. The first point in each curve following zero time and following the rest periods was obtained by stretching the rubber strip ten times by hand. The other points were obtained after stretching the sample by a machine whose frequency was 400 cycles per minute. Each measurement was made 1 minute after flexing stopped. The recovery of resistivity after a long period of rest is shown by the zero time points of the curve. The recovery of resistivity for shorter periods after flexing is shown in Figure 5.

Several other interesting phenomena, previously unreported or incompletely described, were found in making resistivity measurements. The effect of voltage

impressed on the sample during measurement was found to be different for different stocks. For at least one stock, of only moderately high resistivity (about 1000 megohm-cm.), the direct-current resistivity decreased by a factor of almost 10 as the voltage was increased from 5 to 1000 volts. No such change was found

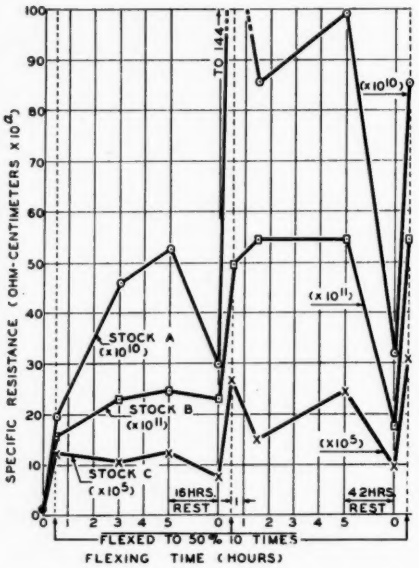

FIG. 4.—Effect of dynamic flexing on specific resistance.

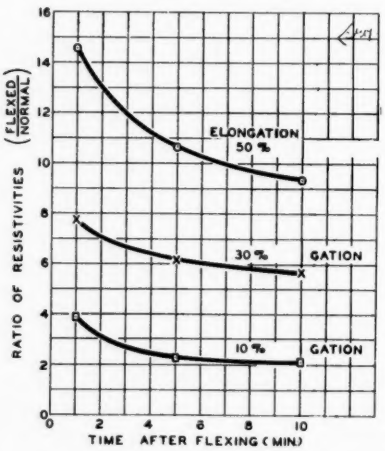

FIG. 5.—Recovery of resistivities after flexing ten times.

for stocks having low resistivities (around 1 megohm-cm. or less), though the measurements were not carried out over so wide a voltage variation in these instances. It would appear from these data, as might be expected, that the stocks having the lowest resistivities behave most like conductors in that their resistivities do not depend on the impressed voltage.

TABLE II

RESISTANCE OF $10.2 \times 15.3 \times 0.25$ CM. TEST SLABS

Compound	Aquadag coating	Pressure on sample (lb./sq. in.)	Resistance in ohms, with electrode material as follows: Copper foil	Copper	Brass	Bright tin	Aluminum	Nickel	Galvanized iron	Cold-rolled steel	Stainless steel
A	None	10	2000	1500	1500	11,000	50,000	8000	12,500	4500	8000
		20	1700	1300	1100	8,000	40,000	5000	7,500	2700	5000
		40	1000	700	650	5,000	25,000	2500	3,500	1700	2700
	Light	10	230	250	250	240	375	250	300	300	320
		20	220	250	220	220	300	230	230	250	250
		40	220	230	220	220	260	230	225	230	230
	Heavy	10	200	200	200	200	210	200	200	220	220
		20	200	200	200	200	210	200	200	210	210
		40	200	200	200	200	210	200	200	210	210
B	None	10	170	100	75	1,500	5×10^4	800	2,000	400	1000
		20	110	50	40	1,000	5×10^4	500	900	250	600
		40	80	35	30	700	5×10^4	350	450	150	350
	Light	10	9	11	7	14	37	17	17	13	17
		20	7	8	6	10	28	11	12	8	12
		40	6.5	7	5.5	8	17	9	9	7	9
	Heavy	10	4.5	5.2	4.2	4.5	7.8	5.0	5.0	5.0	5.5
		20	4.0	4.2	4.0	4.0	5.8	4.3	4.3	4.2	5.0
		40	4.1	4.2	4.0	4.1	5.2	4.1	4.2	4.2	4.5
C	None	10	330[a]	280[a]	320[a]	2,000[a]	5,000[a]	1600[a]	1,700[a]	1100[a]	1400[a]
		20	220[a]	154[a]	170[a]	500[a]	1,500[a]	300[a]	400[a]	350[a]	400[a]
		40	130[a]	120[a]	110[a]	400[a]	900[a]	220[a]	200[a]	180[a]	220[a]
	Light	10	20[a]	22[a]	20[a]	18[a]	23[a]	18[a]	21[a]	21[a]	22[a]
		20	19[a]	20[a]	19[a]	18[a]	21[a]	18[a]	19[a]	19[a]	20[a]
		40	19[a]	20[a]	20[a]	18[a]	21[a]	18[a]	20[a]	20[a]	22[a]
	Heavy	10	13.5[a]	14.0[a]	14.0[a]	14[a]	14[a]	14[a]	14[a]	14[a]	14.2[a]
		20	14.0[a]	14.5[a]	13.9[a]	14.2[a]	15.5[a]	14.5[a]	14.5[a]	14.5[a]	14.6[a]
		40	15.0[a]	15.5[a]	15.0[a]	15[a]	15.0[a]	15.5[a]	15.7[a]	15.2[a]	16.0[a]

[a] $\times 10^3$.

In several cases where available instruments permitted a comparison, the alternating-current resistivities appeared to be generally higher than the direct-current by as much as 25 per cent.

The effects of electrode materials and pressure on electrodes during measurement of resistivity were found to be considerable for stocks of either high or low resistivities. As Table II shows, both of these effects can be substantially eliminated by use of moderate pressures and sufficiently heavy coatings of Aquadag.

The thickness of the Aquadag coating could be controlled by the use of a spraying technique. The commercial Aquadag suspension was thinned out by adding 150 cc. of water, 3000 cc. of alcohol, and 6 cc. of wetting agent (Tergitol) 7 to 300 grams of Aquadag. The resulting suspension was passed through a colloid mill to eliminate lumps. An ordinary spray gun was used to spray the suspension on the rubber samples. During the spraying operation the samples were placed in a metal jig which served as a template for forming the guard-ring electrodes. This method was very convenient for rapidly building up the Aquadag surface

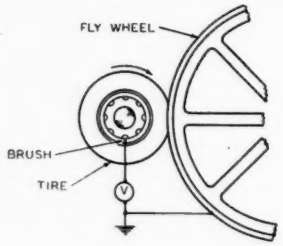

FIG. 6.—Apparatus for indoor drum tests.

TABLE III

COMPARISON OF ROAD TESTS WITH INDOOR DRUM TESTS

Tire	A	B	C	D	E	F	G	H	I	J	K	L
Potentials (percentage of control)												
Of car (road tests).....	39	39	44	56	59	64	81	87	80	82	109	73
Of rim (drum tests).....	41	73	76	58	56	60	88	87	79	74	86	70

to any desired thickness. Some tests have been made on brass electrodes cured directly to the rubber stock. The results so far obtained fail to show any significant difference between the resistivity measured by cured-on electrodes and that measured with similar electrodes on surfaces adequately treated with Aquadag and with the use of moderate electrode pressures.

During the winter it was impossible to make road tests on tires. The tests were then continued on an indoor, 6-foot, steel-drum, tire-testing machine. The tire was mounted on an insulated wheel, and a brush contact with the rim was the collector for the electrostatic voltmeter. Figure 6 is a diagram of the apparatus. The drum was run at a peripheral speed of 30 m. p. h., and a load of 1200 pounds was applied to the 6.00×16 test-tires. When the voltmeter reading reached a constant value, the voltage was recorded.

The results of Table III show good correlation between the indoor and the outdoor tests, except for tires B and C. In the tests on tires B and C, only one tire out of each set of four used for the outdoor tests was available for the indoor tests. Consequently, the discrepancy between the indoor and the outdoor tests in these cases may have been due to an abnormal variation in the tires themselves.

ELECTRICAL SHOCK

The problem of shock hazard to a passenger leaving or entering a motor vehicle depends on the potential retained on the vehicle after it stops. The steps taken to reduce tire radio static by reducing the potential generated by the tires therefore also reduce the shock hazard. Tires having a low rim-to-tread resistance would be especially effective in reducing the danger of electrical shock. This conclusion is in contradiction to statements made in a recent publication[1]:

Beach dismissed, apparently without trial, the possibility of reducing the shock hazard by the use of low-resistivity tires. However, the writers have found by direct experiment that, when the high resistivity tires on busses, which gave static trouble in service, were replaced by low-resistivity tires, the shock hazard was eliminated.

Beach's argument that the high resistivity of pavements would nullify any attempt to solve the problem by the use of low resistivity tires is not convincing. As an example of the high resistance of pavements, he cites the value of 2000 megohms measured between ground and an unspecified electrode on the pavement surface. Let us assume that the resistance to ground of a bus is of that order of magnitude. The bus capacitance is given by Beach as approximately 1000 micromicrofarads. When these values are substituted in the well-known equation for the discharge of a condenser, it is found that the bus will lose in only 2 seconds about two-thirds of its voltage, and in 6 seconds about 95 per cent of its original voltage. Evidently, then, the tire resistance must have played some part in causing the condition which allowed the bus reported by Beach to retain a high potential for several hours after stopping. The writers' experience has been that, whenever such a phenomenon occurred, the bus was always equipped with tires of exceptionally high resistivity. High-resistance pavements, therefore, are only one factor in the problem.

Beach seems to pin his hope for the complete elimination of tire static on the development of low-resistivity pavements. However, this would be no solution at all unless low-resistivity tires were also used.

Another statement in Beach's paper which appears erroneous is that "only under certain meteorological conditions" does a vehicle become charged by conduction. To arrive at that conclusion, Beach must have confined his experiments to very high-resistivity tires. Some charge will leak through the best of insulators; consequently, even with tires of exceptionally high resistance the vehicle must be charged, at least in part, by conduction through its tires. After the vehicle has been in motion for a matter of hours, it will become wholly charged by conduction even though equipped with exceptionally high-resistance tires.

In addition, it is obvious that artificial means of grounding the car on stopping would eliminate the danger of shock. For example, some toll bridges are provided with flat springs, projecting through the pavement, which make contact with the car as it stops before the tollhouse.

The problem of electrical shock is especially important to aviation transportation. It is well known that the potential gradient near the earth's surface is 60-300 volts per meter and that, in flight, an airplane eventually acquires the same potential as the surrounding atmosphere. On landing, the airplane might therefore be at a highpotential with respect to the ground. To permit the airplane to be brought back to ground potential before the passengers step out, highly conducting tail-wheel tires have been developed. Some of these have rim-to-tread resistances of 2000 to 10,000 ohms as compared to about 10^{10} ohms for ordinary tires.

THEORY

When the problem was begun, several theories had been proposed for explaining how a static charge accumulated on the car. Among these theories were the following: (1) The car became charged by air friction; (2) dust particles became charged at the tire tread and, on reaching the car fender, gave up that charge; (3) ions were formed in the exhaust gases and, on escaping from the exhaust pipe, left the car with a net charge; and (4) the charge generated at the tire tread reached the rim by conduction over the tire side walls. The last theory was given most credence; the first three were disposed of by direct experiment.

However, a difficulty with theory *d* arose when it was found that tires having a low side-wall resistance usually developed a low car potential. From a naive consideration of the theory, one might expect the opposite to be true.

Consequently, an experiment was performed to map the potential gradients over the surface of a tire running at 30 m. p. h. on the indoor testing drum. A probe was made from a strong polonium-plated foil 3 cm. in diameter, bent into a cone whose base was 1 cm. in diameter. This probe was well insulated, and was

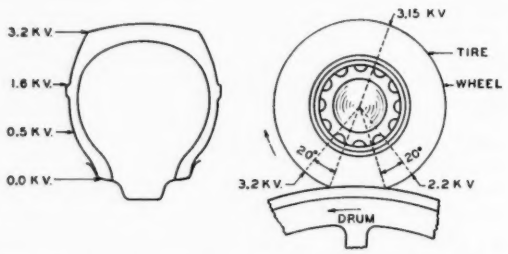

FIG. 7.—Potentials on surface of tire running on steel drum.

connected to a low-sensitivity electroscope whose case was grounded. When the probe was held about 1 cm. from the moving tire surface, the electroscope leaf attained a steady value within 1 minute. The reading was recorded after 1.5 minutes at each position of the tire investigated. The results of this investigation are shown in Figure 7. Aside from the expected result that the tire tread was at a high potential, even when the rim was grounded, the most striking result was the large difference in tread potential which existed between the regions where the tread approached and where it left the drum contact area.[14] Obviously, the electric charge was generated when the tire pulled away from the drum.

The data shown in Figure 7 indicate that the charge generated at the tread surface leaks over the side wall to the rim. It is probable that some charge escapes from the rim by leakage over the side wall to the drum contact area, and this would account for the low potential observed on a car with high-conductivity side wall tires. The probable direction of the currents in a tire running on a pavement are indicated in Figure 8.

The following derivation of the equilibrium rim voltage is based on the above principles and, in addition, on the assumption that the tread potential depends only on the charge density. This may not be true in practice because of the proximity of conductors (fenders) to the tire. However, it is felt that the equa-

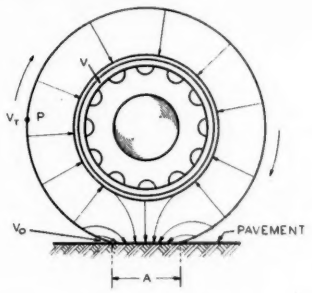

FIG. 8.—Direction of electric currents in rotating tire.

tion is qualitatively correct in that it agrees with the experimentally observed dependence of rim potential on the variables in the problem:

Let C = tread to rim conductivity per unit length of tire periphery
σ = electrostatic charge per unit length of tire periphery
$K\sigma = V_T$ = potential at any point P of tire periphery
V = rim potential
A = length of tire pavement contact
$A+B$ = circumference of tire
v = velocity of tire periphery

At point P the current per unit length flowing to the rim is:

$$(K\sigma - V)C = -\frac{d\sigma}{dt}$$

and

$$t = \int_{\sigma_0}^{\sigma} \frac{-d\sigma}{(K\sigma - V)C} = -\frac{1}{KC} \log \frac{K\sigma - V}{K\sigma_0 - V}$$

where t = time required for tread to travel a distance l from pavement to point P

σ_0 = charge per unit length in region where tire pulls away from pavement

Now $t = l/v$, so that the potential difference between the rim and the point P is:

$$(K\sigma - V) = (K\sigma_0 - V)e^{-\frac{KCl}{v}}$$

It follows that the total current to rim is:

$$i_c = C\int_0^B (K\sigma_0 - V)e^{-\frac{KCl}{v}}\, dl$$

or

$$i_c = -C(K\sigma_0 - V)\frac{v}{KC}\left(e^{-\frac{KCB}{v}} - 1\right)$$

The total current flowing from rim to ground is $i_d = CAV$.

At equilibrium $i_c=i_d$, or

$$V=\frac{v\sigma_0\left(1-e^{-\frac{KCB}{v}}\right)}{CA+\frac{v}{K}\left(1-e^{-\frac{KCB}{v}}\right)}$$

The equation agrees with the experimentally known fact that the rim potential increases with an increase in the velocity and the tread-to-rim resistivity. In addition, it predicts that the rim voltage should decrease with an increase in the pavement contact length, A. This effect was also experimentally observed, since the rim voltage was found to increase with increased tire inflation and to decrease with increased tire load.

The equation indicates that the minimum rim potential, $V=0$, could be expected for $C=\infty$. The maximum rim potential (for $C=0$) would be:

$$V=K\sigma_0\frac{B}{A+B}$$

Therefore, if σ_0 is assumed to be constant for all tires, a lowering of the car potential at any given speed could be accomplished by reducing the rim-to-tread resistance of the tires.

ACKNOWLEDGMENT

The authors are indebted to J. N. Street and J. H. Dillon for their constant interest and many helpful discussions, and to Frank S. Grover, who constructed the static machine shown in Figure 1. Thanks are due also the Compounding and Development Departments for their coöperation in certain phases of this work, and to The Firestone Tire & Rubber Company for permitting the work to be published.

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[14] The tread potential distribution shown in Figure 7 is in disagreement with the one presented by Cadwell, Handel, and Benson [*News Ed.* (*Am. Chem. Soc.*) **19**, 1139, Fig. 3 (1941)]. In the discussion following their paper at the Atlantic City meeting of the AMERICAN CHEMICAL SOCIETY, W. F. Busse, who has given us permission to quote him, presented data on equilibrium tread potential distributions which also disagreed with that shown in Figure 3 of Cadwell *et al.* but agrees in general form with the distribution shown in our Figure 7. Furthermore, the data presented by Busse indicated that these tread potential distributions were not greatly affected by introducing into the inner tube either conducting liquids or conducting powders such as the "static neutralizer" discussed by Cadwell *et al.* As mentioned at that time, these data, comprising measurements made over more than half of the tire circumference, agreed in general with the results of similar tests we had made previous to the meeting. Busse also reported that the introduction of a conducting liquid or conducting powder to the inner tubes of all four tires on a car had no appreciable effect on the equilibrium potential of the car when driven along the road or on the radio static generated by the discharge of the potential. Tests conducted on a tire mounted on an insulated wheel in our laboratory similarly failed to show any diminution in the equilibrium potential of this insulated wheel as a result of applying the "neutralizer". Tests made subsequent to those discussed above have indicated that the "neutralizer" does affect somewhat the tread potential distribution of a tire

running on an insulating surface. It is important to add, however, that, even under these conditions, no significant diminution in the equilibrium potential of the insulated wheel on which the tire was mounted has ever been found. Since this potential corresponds to that found on the car body in service, it is difficult to reconcile these results, and those Busse obtained independently, with the rather inclusive claims made for the "neutralizer" of Cadwell and coworkers.

The data presented by Busse also showed that, when one of four high-resistance tires was replaced by a tire of relatively low resistance, the potential of the car was reduced. The assertion by Cadwell and his collaborators that the obvious solution to the problem, *i.e.*, to make the tires electrically conducting, has consistently proved unsatisfactory, disagrees also with our experience. Thousands of tires built with rubber compounds having relatively low resistivity, but otherwise similar to "regular" tires, have been substituted for such regular tires in regions where shock static has been most objectionable. The use of these low-resistance tires has resulted in a complete elimination of the static shock problem in these localities.

Semiconducting stocks have been employed with similar success in many applications important in our defense effort, such as the manufacture of static-free industrial tires (both solid and pneumatic) for trucks in munitions plants and oil refineries, airplane tires, etc.

[15] The term "frictional" process may be objectionable to some workers in the field of static electricity since a difference of opinion exists about the mechanism of charge separation. Experiments were performed which showed that a charge separation occurred when two materials were placed in intimate contact even without rubbing and were then separated. Whether it is possible to place two materials in intimate contact without some wiping effect is questionable. Beach[1] contends, without citing any experimental evidence, that the phenomenon should be described in terms of contact differences of potential. In the writers' opinion, the question of whether the process is called frictional electrification or contact difference of potential is not fundamental to methods of attacking the problem.